

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
22 April 2004 (22.04.2004)

PCT

(10) International Publication Number  
**WO 2004/034445 A2**

(51) International Patent Classification<sup>7</sup>: **H01L 21/00**

(21) International Application Number:  
PCT/US2003/031712

(22) International Filing Date: 6 October 2003 (06.10.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/417,806 11 October 2002 (11.10.2002) US  
10/295,601 14 November 2002 (14.11.2002) US  
10/674,675 29 September 2003 (29.09.2003) US

(71) Applicants (for all designated States except US): **LAM RESEARCH CORPORATION** [US/US]; 4650 Cushing Parkway, Fremont, CA 94538 (US). **LI, Lumin** [US/US]; 3480 Tracy Drive, Santa Clara, CA 95051 (US). **SAD-JADI, Reza** [US/US]; 19413 Vineyard Lane, Saratoga, CA 95070 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **HUANG, Zhisong** [US/US]; 5972 Roxie Terrace, Fremont, CA 94555 (US).

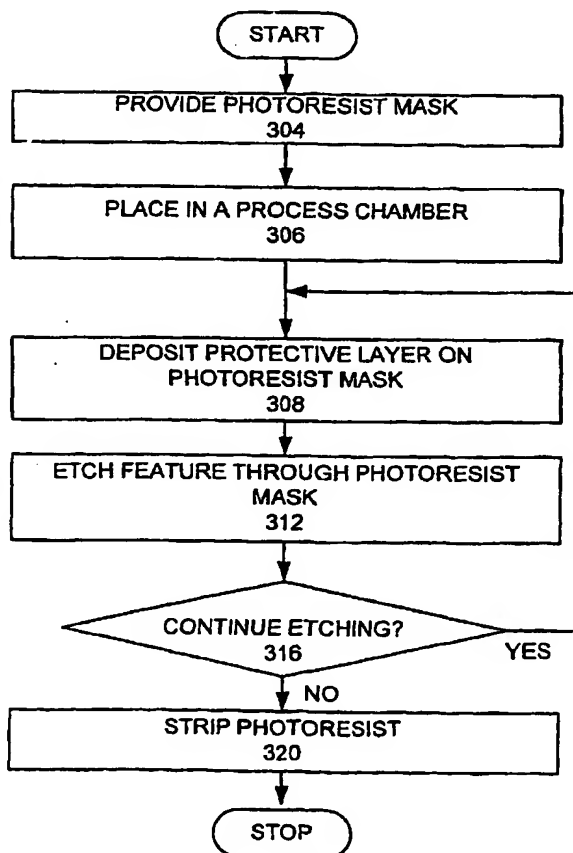
(74) Agent: **OLYNICK, Mary, R.**; Beyer Weaver & Thomas, LLP, P.O. Box 778, Berkeley, CA 94704-0778 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,

[Continued on next page]

(54) Title: A METHOD FOR PLASMA ETCHING PERFORMANCE ENHANCEMENT



(57) Abstract: A method for etching a feature in a layer through an etching mask is provided. A protective layer is formed on exposed surfaces of the etching mask and vertical sidewalls of the feature with a passivation gas mixture. The feature is etched through the etching mask with reactive etching mixtures containing at least one etching chemical and at least one passivation chemical.

WO 2004/034445 A2



SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**Published:**

- *without international search report and to be republished upon receipt of that report*

## A METHOD FOR PLASMA ETCHING PERFORMANCE ENHANCEMENT

### BACKGROUND OF THE INVENTION

#### 5 1. Field of the Invention

The invention relates to a method of obtaining a structure on a semiconductor wafer by etching through structures defined by an etch mask using a plasma.

#### 2. Description of the related art

In semiconductor plasma etching applications, a plasma etcher is usually used to transfer a photoresist mask pattern into a circuit and line pattern of a desired thin film and/or filmstack (conductors or dielectric insulators) on a Si wafer. This is achieved by etching away the films (and filmstacks) underneath the photoresist materials in the opened areas of the mask pattern. This etching reaction is initiated by the chemically active species and electrically charged particles (ions) generated by exciting an electric discharge in a reactant mixture contained in a vacuum enclosure also referred to as a reactor chamber. Additionally, the ions are also accelerated towards the wafer materials through an electric field created between the gas mixture and the wafer materials, generating a directional removal of the etching materials along the direction of the ion trajectory in a manner referred to as anisotropic etching. At the finish of the etching sequence, the masking materials are removed by stripping it away, leaving in its place replica of the lateral pattern of the original intended mask patterns. This etching method is illustrated in FIG.'S 1A-C. In this method, a plasma etching process is used to transfer directly the photoresist mask pattern 104 into that of the underlying oxide dielectric thin film 108, as shown in FIG. 1A. The etching generates a contact hole 112 and erodes and damages the photoresist 104, as shown in FIG. 1B. The photoresist is then removed leaving the contact hole 112 in the oxide 108, as shown in FIG. 1C. During the etching process, the mask materials are usually eroded and/or damaged in exchange for the pattern transfer. Consequently, some of the damage and erosion also may be transferred to the underlying layers leaving such undesirable pattern distortions such as striation, CD enlargement, etc.

The objective of the etching methodology, therefore, includes reducing the photoresist mask erosion to enhance the fidelity of the pattern transfer from the photoresist mask patterns. For this purpose, it has been proposed to include a passivation gas in the reactive etching mixture. This passivation gas can be chosen in such a way that its presence selectively reduces the etching damage and erosion of the masking materials relative to the removal rate of the thin film materials to be etched. The passivation gas can be chosen in such a way that,

an etching retardation coating is generated on the surface of the masking materials acting as a barrier to slow down the etching reaction. By design, the passivation gas is chosen in a way that it additionally beneficially forms an etching retardation coating on vertical surfaces of the film structures to be etched, such that etching reaction cannot advance in the absence of the ion bombardment. By the nature of the vertical trajectory of the charged particles, etching can therefore advance only in the vertical direction, with little to no etching in the lateral direction, creating an anisotropic etching profile. Hence, the presence of a passivation gas in the etching mixture is very important for the advantage of better etching mask protection and highly anisotropic etching profile by the use of relatively high energy directional ion bombardment.

It has already been proposed that the reactive gas mixture contain etching gases and polymer formers, with the latter acting the role of a passivation gas. In this case, the etching gases release highly reactive species by the excitation of an electrical discharge, which in turn etches the thin film materials to be etched as well as the masking materials by the mechanism of a spontaneous reaction. By the nature of spontaneous reactions, the etching reaction advances in both the vertical as well as the lateral surfaces, creating isotropic etching profiles. The co-presence of a polymer former, through generation of a polymer deposit on the surface of the etching structures and masking materials, can be used to create simultaneously high etching selectivity to masking materials and etching anisotropy, in conjunction with the ion bombardment.

It also has already been proposed that the reactive gas mixture contain polymer former gases and an etching enabler gas. The role of the etching enabler gas is to enable the polymer former gas to release highly reactive species by reacting with the polymer former gases in the presence of an electrical discharge. Alternatively, a retardation coating on the etching materials as well as the masking materials can also be formed by chemical reaction of a properly chosen passivation gas directly with the surfaces of these materials.

A common disadvantage of the above mentioned methods is that the optimum conditions for different aspects of the etching requirement usually do not coincide and by mixing the gases some of the unique properties of each precursor gases may be lost due to inter-reactions. The etching condition optimization almost always involve complex trade-offs into a single etching condition that may not be the optimum should the different etching chemistries be separate.

A variant of the etching methodology is taught in U.S. Patent 5,501,893, issued March 26, 1996 to Laermer et al., entitled "Method of Anisotropically Etching Silicon". This method separates out the etching gases and polymer former gases into two different steps, each

consisting purely of one type of chemicals but not the other. This allows for fast etching rate at low ion bombardment energies, since at low ion bombardment energies, high selectivities to masking materials can be achieved for certain spontaneous etching reactions if the activation energy is slightly lower for the reaction at the surface of the etching materials than the masking materials. By removing the polymer former from the etching process, on the other hand, the etching process would necessarily be isotropic during the duration when the etching is proceeding, since there is no retardation layer to prevent the lateral etching from occurring. Additionally, without the passivation gas in the etching mixture, it would be difficult to obtain sufficient etching selectivity to the masking materials if the desire is there to use higher ion energies. Many etching applications can benefit from high ion bombardment energy to obtain high aspect ratio structures in very small dimension structures, for example.

Additional proposed methods include a stacked masking scheme to improve the overall etching resistance of the masking materials. This is illustrated in FIG.'S 2A-F. In FIG. 2A an oxide layer 204 is provided. FIG. 2B shows a hardmask layer 208 placed over the oxide layer. A photoresist mask 212 is placed over the hardmask layer 208, as shown in FIG. 2C. The photoresist mask 212 is used to pattern the hardmask layer 208 to create a patterned hardmask layer 214, and the photoresist layer 212 may be removed, as shown in FIG. 2D. A contact hole 216 is etched in the oxide layer 204, using the patterned hardmask layer 214 as a mask as shown in FIG. 2E. The hardmask is then removed leaving the contact 216 in the oxide layer 204, as shown in FIG. 2F.

The advantages of this method are that, by having a more inert hardmask from which to transfer patterns (circuits and lines) to the underlying films, the etch performance is much enhanced and the requirement on the etching and photolithography is also much reduced. The disadvantages of this method are that, by introducing new process steps and new tool sets into the process flow, it is of higher cost and lower overall throughput. In addition, the extra process complexity also introduces difficulties by itself. For example, the Si hardmask used for dielectric contact etch applications is not as easily stripped as the photoresist mask.

In addition to transfer without lateral CD loss or damage the mask pattern into the etch layer, the lateral CD of a lateral pattern already present in the etch layer may also need to be preserved in many etching applications during the process of etching the etch layer. These etch layer patterns are usually not protected by the etching mask materials. A discussion of this class of etching applications is given using the example of a formation of a dual damascene structure by plasma etching.

To facilitate discussion, FIG. 9A is a cross-sectional view of a stack 900 on a wafer 110 used in the dual damascene process of the prior art. A contact 904 may be placed in a dielectric layer 908 over a wafer 910. A barrier layer 912, which may be of silicon nitride or silicon carbide, may be placed over the contact 904 to prevent the copper diffusion. A via level silicon oxide dielectric layer 916 may be placed over the barrier layer 912. A trench stop layer 920 (silicon carbide or silicon nitride) may be placed over via level dielectric 916. A trench level silicon oxide dielectric layer 924 may be placed over the trench stop layer 920. An antireflective layer (ARL) 928 may be placed over the trench dielectric layer 924. A patterned resist layer 932 may be placed over the ARL 928. The ARL 928 may be formed from silicon nitride, SiON, or other material with a high refractive index and high extinction coefficient.

FIG. 10 is a high level flow chart of a process used in the prior art to form the stack 900 into a dual damascene structure. The stack 900 may be subjected to an etch, which etches a via 940 down to the barrier layer 912 (step 1004). The etching of the via 940 may form a crust 944, which forms sidewalls. The crust 944 and resist 932 may be removed and subsequently repatterned with a new resist layer 960, which is patterned to form a trench (step 1008), as shown in FIG. 9C. The stack may be subjected to an etch, which etches a trench 964 down to the intermediate trench etch stop layer 920 (step 1012), as shown in FIG. 9D. The etching of the trench 964 may cause part of the via level dielectric layer 916 to facet 972. This faceting may be considered as damage to the dual damascene structure. The intermediate trench etch stop layer 920 may be used to reduce faceting. The etching of the trench 964 may also form a new crust 968, which forms sidewalls. The resist layer 160 and crust may then be stripped (step 1016). The stack 900 may then be subjected to a barrier layer etch (step 1020), which opens the via 940 to the copper contact 904, to provide the structure shown in FIG. 9E. A metal barrier layer 974 may be deposited over the copper contact (step 1024), as shown in FIG. 9F. A copper seed layer 976 may then be used to coat the interior of the via and trench. Electroplating may be used to fill the trench and via with copper 978, which is polished down to the trench dielectric layer 924. The copper 978 may be used as a copper connect for the next level, so the process is repeated creating multiple levels of copper connects and dielectric layers.

Although the intermediate trench etch stop layer may be used to reduce faceting, providing and etching the intermediate trench etch stop layer requires additional processing steps, which increases processing time and costs.

In addition, integrated circuits use dielectric layers, which have typically been formed from silicon dioxide, SiO<sub>2</sub>, to insulate conductive lines on various layers of a semiconductor structure. As semiconductor circuits become faster and more compact, operating frequencies increase and the distances between the conductive lines within the semiconductor device decrease. This introduces an increased level of coupling capacitance to the circuit, which has the drawback of slowing the operation of the semiconductor device. Therefore, it has become important to use dielectric layers that are capable of effectively insulating conductive lines against such increasing coupling capacitance levels.

In general, the coupling capacitance in an integrated circuit is directly proportional to the dielectric constant,  $k$ , of the material used to form the dielectric layers. As noted above, the dielectric layers in conventional integrated circuits have traditionally been formed of SiO<sub>2</sub>, which has a dielectric constant of about 4.0. As a consequence of the increasing line densities and operating frequencies in semiconductor devices, dielectric layers formed of SiO<sub>2</sub> may not effectively insulate the conductive lines to the extent required to avoid increased coupling capacitance levels.

In an effort to reduce the coupling capacitance levels in integrated circuits, the semiconductor industry has engaged in research to develop materials having a dielectric constant lower than that of SiO<sub>2</sub>, which materials are suitable for use in forming the dielectric layers in integrated circuits. A number of promising materials, which are sometimes referred to as "low- $k$  materials," have been developed. In the specification and claims, low- $k$  materials are defined as materials with a dielectric constant  $k$  that is less than 4. Fluorosilicate glass is one example of a low- $k$  dielectric, which has a dielectric constant of about 3.7. This composes an about 7-9% fluorine doped into SiO<sub>2</sub>.

Another interesting class of low- $k$  materials is compounds including organosilicate glass, or OSG. By way of example, but not limitation, such organosilicate dielectrics include CORAL™ from Novellus of San Jose, California; Black Diamond™ from Applied Materials of Santa Clara, California; Aurora™ available from ASM International N.V., The Netherlands; Sumika Film® available from Sumitomo Chemical America, Inc., Santa Clara, California, and HOSP™ from Allied Signal of Morristown, New Jersey. Organosilicate glass materials have carbon and hydrogen atoms incorporated into the silicon dioxide lattice which lowers the

density, and hence the dielectric constant of the material. A dielectric constant for such films is typically  $< 3.0$ .

To facilitate discussion, FIG. 11A is a cross-sectional view of part of a wafer in the production of a damascene structure without a trench stop layer and using a low-k dielectric. A contact 1104 may be placed in a low-k dielectric layer 1108 over a wafer 1110. A second contact 1106 may also be in the low-k dielectric layer 1108. A dielectric barrier layer 1112, typically, but not limited to, silicon nitride or silicon carbide, may be placed over the contact 1104 to prevent copper diffusion. A low-k dielectric layer 1120 may be placed over the barrier layer 1112. An antireflective layer (ARL) 1128 may be placed over the low-k dielectric layer 1120. A patterned resist layer 1132 may be placed over the ARL 1128. The patterned resist layer 1132 is patterned to provide a via 1140, which is etched into the low-k dielectric layer 1120. The resist layer 1132 is removed and a second patterned resist layer 1160 is placed over the ARL 1128, as shown in FIG 11B.. The second resist layer 1160 is patterned to provide a trench 1164, which is etched into the low-k dielectric layer 1120.

Because of the absence of the intermediate trench etch stop layer and the use of a low-k dielectric, faceting 1172 in this example may be increased. Such faceting may cause the copper, which would be used to fill in the via and trench, to be too close to the second contact 1106. This may also increase the dimension of the bottom of the via.

To facilitate understanding, FIG. 12A is a cross-sectional view of part of a wafer in the production of a damascene structure without a trench stop layer and using a low-k dielectric. A first contact 1204 and a second contact 1206 may be placed in a low-k dielectric layer 1208 over a wafer 1210. A dielectric barrier layer 1212, typically, but not limited to silicon nitride or silicon carbide, may be placed over the first and second contacts 1204, 1206 to prevent the copper diffusion. A low-k dielectric layer 1220 may be placed over the barrier layer 1212. First 1240 and second 1244 vias may be etched into the low-k dielectric layer 1220. A bottom antireflective coating (BARC) layer 1228 may be spun over the low-k dielectric layer 1220. Such a spun on BARC tends to at least partially fill the vias 1240, 1244 and form sidewalls and plugs in the vias. Generally, thinner vias are filled with BARC to a higher depth than wider vias are filled. Also, more spread apart vias may be filled higher than more closely packed vias. As a result, it may be difficult to have the vias filled to a uniform height.



FIG. 12B is a cross-sectional view of part of the wafer after trenches 1248, 1252 have been etched. The presence of BARC in the vias creates fences 1256, 1260 and, in addition, faceting 1262, 1264. The amount of faceting and the size of the fences are dependent on the height of the BARC. Therefore, non-uniform BARC height may cause non-uniform faceting and fences. The fences may be a stress location, which may cause electro-migration, voids and other failures, which may diminish the reliability of the resulting semiconductor devices.

In addition, plug filling and stripping adds additional costs and complexity to the process flow. In addition, such plugs may cause dielectric poisoning in upcoming dielectric materials. Without plug fillings it may be difficult to prevent and increase in CD of via holes due to erosion by mechanisms, such as faceting. The purpose of this invention is to provide a generic method for etching a feature in a layer or a stack of layers to obtain a high fidelity replica of a lateral pattern formed by a masking material with simultaneously high etching anisotropy and high selectivity to the masking materials as well as to the stop layers. Additionally, this invention intends to provide a generic method for etching a lateral pattern already present in the etch layer that is not covered by the etching mask and not protected or insufficiently protected by a sacrificial filler material, without unduly lateral CD loss and damage to the etch layer lateral patterns.

## SUMMARY OF THE INVENTION

To achieve the foregoing and in accordance with the purpose of the present invention, a method for etching a feature in a layer through an etching mask is provided. A protective layer is formed on exposed surfaces of the etching mask and vertical sidewalls of the feature with a passivation gas mixture. The feature is etched through the etching mask with reactive etching mixtures containing at least one etching chemical and at least one passivation chemical.

In another embodiment of the invention, an apparatus for etching a layer under an etch mask, where the layer is supported by a substrate, is provided. A plasma processing chamber comprising a chamber wall forming a plasma processing chamber enclosure, a substrate support for supporting a substrate within the plasma processing chamber enclosure, a pressure regulator for regulating the pressure in the plasma processing chamber enclosure, at least one electrode for providing power to the plasma processing chamber enclosure for sustaining a plasma, a gas inlet for providing gas into the plasma processing chamber enclosure, and a gas outlet for exhausting gas

from the plasma processing chamber enclosure is provided. A deposition gas source and an etchant gas source are provided. A first control valve in fluid connection between the gas inlet of the plasma processing chamber and the deposition gas source and a second control valve in fluid connection between the gas inlet of the plasma processing chamber and the etchant gas source are provided. A controller controllably connected to the first control valve, the second control valve, and the at least one electrode comprising at least one processor and computer readable media is provided. The computer readable media comprises computer readable code for opening the first control valve for at least one deposition step to provide a deposition gas from the deposition gas source to the plasma processing chamber enclosure, computer readable code for closing the second control valve for the at least one deposition step to prevent etching gas from the etching gas source from entering the plasma processing chamber enclosure, computer readable code for opening the second control valve for at least one etching step to provide an etching gas from the etching gas source to the plasma processing chamber, and computer readable code energizing the at least one electrode to provide a bias of greater than 250 volts on the substrate for at least one etching step.

In another embodiment of the present invention, a method for forming a dual damascene feature is provided. Vias are formed in an etch layer. A trench patterned mask is provided over the etch layer. A trench is etched, where the etching the trench comprises a cycle of forming protective sidewalls over the sidewalls of the vias and etching a trench through the trench patterned mask. The mask is then stripped.

In another manifestation of the invention an apparatus for etching a layer under an etch mask, wherein the layer is supported by a substrate is provided. A plasma processing chamber is provided. The plasma processing chamber comprises a chamber wall forming a plasma processing chamber enclosure, a substrate support for supporting a substrate within the plasma processing chamber enclosure, a pressure regulator for regulating the pressure in the plasma processing chamber enclosure, at least one electrode for providing power to the plasma processing chamber enclosure for sustaining a plasma, a gas inlet for providing gas into the plasma processing chamber enclosure, and a gas outlet for exhausting gas from the plasma processing chamber enclosure. A deposition gas source and an etchant gas source are provided. A first control valve is in fluid connection between the gas inlet of the plasma processing chamber and the deposition gas source. A second control valve is in fluid connection between the gas inlet of the plasma processing chamber and the etchant gas

source. A controller is controllably connected to the first control valve, the second control valve, and the at least one electrode. The controller comprises at least one processor and computer readable media. The computer readable media comprises computer readable code for opening the first control valve for at least one deposition  
5 step to provide a deposition gas from the deposition gas source to the plasma processing chamber enclosure, computer readable code for closing the second control valve for the at least one deposition step to prevent etching gas from the etchant gas source from entering the plasma processing chamber enclosure, and computer readable code for opening the second control valve for at least one etching step to provide an  
10 etching gas from the etchant gas source to the plasma processing chamber.

These and other features of the present invention will be described in more details below in the detailed description of the invention and in conjunction with the following figures.

15

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

The present invention is illustrated by way of example, and not by way of limitation, in the figures of the accompanying drawings and in which like reference numerals refer to similar elements and in which:

FIG.'S 1A-C are schematic views of the formation of a contact hole feature  
20 through a prior art process.

FIG.'S 2A-F are schematic views of the formation of a contact hole feature through another prior art process.

FIG. 3 is a flow chart of an inventive passivation and etch process.

FIG.'S 4A-F are schematic views of the formation of a contact hole using the  
25 inventive process.

FIG. 5 is a schematic view of a system that may be used in practicing the invention.

FIG. 6 is a micrograph of a plurality of high aspect ratio contact hole patterns formed using the invention.

FIG. 7 is a micrograph of a plurality of high aspect ratio contact hole patterns formed using a prior art process.  
30

FIG.'S 8A-B are schematic views of a computer system that may be used in practicing the invention.

FIG.'s 9A-F are a cross-sectional views of a stack on which a dual damascene feature is formed using prior art processes.

FIG. 10 is a high level flow chart of a process used in the prior art to form a dual damascene structure.

5        FIG.'s 11A-B are cross-sectional views of part of a wafer in the production of a damascene structure without a trench stop layer and using a low-k dielectric, according to a prior art process.

10        FIG.'s 12A-B is a cross-sectional view of part of a wafer in the production of a damascene structure without a trench stop layer and using a low-k dielectric according to another prior art process.

FIG. 13 is a high level flow chart for an example for forming a dual damascene feature using a via first scheme.

FIG.'s 14A-E are a cross-sectional views of part of a substrate over into which a dual damascene structure is formed.

15        FIG. 15A is a photomicrograph of a cross-sectional view of a dual damascene feature that has been etched according to the invention.

FIG. 15B is a top and side perspective view of the dual damascene feature.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

20        The present invention will now be described in detail with reference to a few preferred embodiments thereof as illustrated in the accompanying drawings. In the following description, numerous specific details are set forth in order to provide a thorough understanding of the present invention. It will be apparent, however, to one skilled in the art, that the present invention may be practiced without some or all of these specific details. In other instances, well known process steps and/or structures have not been described in detail in order to not unnecessarily obscure the present invention.

30        The said invention is a new etching method in which an *in-situ* passivation process is combined and integrated with an etch process to enhance the overall etch performance without unduly sacrificing simplicity and cost-effectiveness.

In this new method, an in-situ plasma chemical process is used to enhance and/or repair the photoresist mask, as well as the vertical sidewalls of etching features, during the etching progression. During this new etch sequence, a plasma chemical process step is initiated for a short duration before and/or after the wafer is exposed to

an etching plasma for a desired duration. The plasma passivation process is chosen in such a way that a thin film of material coatings is formed on the mask pattern to protect the mask from later etch erosion. Preferably, this thin coating is of a material that is compatible with later stripping process for ease of final removal but more etch resistant than the mask materials. For example, a carbon-rich thin film, containing very low to no amount of other elements, can be used to coat a photoresist mask so that protected mask features is not easily eroded by the subsequent etching process. In other words, it changes the surface composition of the mask pattern such that the mask behaves like a pseudo hardmask, having certain beneficial etching characteristics of an amorphous carbon hardmask. Alternatively, the passivation process may also be used in such a way that the formation of the thin coating on the mask pattern largely compensates for and/or repairs the mask patterns damaged/eroded by the prior etch process. The relative inertness of the coating to the subsequent etching reaction is beneficial so as to not to alter the fine balance obtained in the etching step.

The etching gas mixture contains etchant species and at least one passivation species so as to not lose the benefits associated with a passivation gas in the etching chemistry. The ratio of the etching to passivation components, along with a plurality of other processing conditions, is finely balanced to achieve optimum processing results, such as photoresist selectivity, etching anisotropy and etching rate etc. The electrical discharge power is kept high and the energy of the charged particles is also kept high to obtain high etch rate and good etching anisotropy in small dimensional structures. The passivation and etching sequence can be, but may not need to be, reiterated and adjusted until the completion of the etching task.

To facilitate understanding, FIG. 3 is a flow chart of an embodiment of the invention. A photoresist mask is provided on a layer to be etched (step 304). FIG.'S 4A-F are schematic illustrations of the process. FIG. 4A shows a photoresist mask 404, which has been provided on an oxide layer 408 to be etched, which is on a substrate. The substrate is placed in a process chamber (step 306).

FIG. 5 is a schematic view of a process chamber 500 that may be used in the preferred embodiment of the invention. In this embodiment, the plasma processing chamber 500 comprises confinement rings 502, an upper electrode 504, a lower electrode 508, a gas source 510, and an exhaust pump 520. The gas source 510 comprises a passivation gas source 512, an etchant gas source 514, and an additional gas source 516. Within plasma processing chamber 500, the substrate wafer 580, on

which the oxide layer is deposited, is positioned upon the lower electrode 508. The lower electrode 508 incorporates a suitable substrate chucking mechanism (e.g., electrostatic, mechanical clamping, or the like) for holding the substrate wafer 580. The reactor top 528 incorporates the upper electrode 504 disposed immediately  
5 opposite the lower electrode 508. The upper electrode 504, lower electrode 508, and confinement rings 502 define the confined plasma volume 540. Gas is supplied to the confined plasma volume by gas source 510 through a gas inlet 543 and is exhausted from the confined plasma volume through the confinement rings 502 and an exhaust port by the exhaust pump 520. The exhaust pump 520 forms a gas outlet for the  
10 plasma processing chamber. A first RF source 544 is electrically connected to the upper electrode 504. A second RF source 548 is electrically connected to the lower electrode 508. Chamber walls 552 define a plasma enclosure in which the confinement rings 502, the upper electrode 504, and the lower electrode 508 are disposed. Both the first RF source 544 and the second RF source 548 may comprise a  
15 27 MHz power source and a 2 MHz power source. Different combinations of connecting RF power to the electrode are possible. A modified Exelan 2300 DFC (Dual Frequency Confined) made by LAM Research Corporation™ of Fremont, California may be used in a preferred embodiment of the invention. A controller 535 is controllably connected to the first RF source 544, the second RF source 548, the  
20 exhaust pump 520, a first control valve 537 connected to the deposition gas source 512, a second control valve 539 connected to the etch gas source 514, and a third control valve 541 connected to the additional gas source 516. The gas inlet 543 provides gas from the gas sources 512, 514, 516 into the plasma processing enclosure. A showerhead may be connected to the gas inlet 543. The gas inlet 543 may be a  
25 single inlet for each gas source or a different inlet for each gas source or a plurality of inlets for each gas source or other possible combinations.

A protective layer 412 is formed on the photoresist mask 404, as shown in FIG. 4B (step 308). It is preferred that the deposition be asymmetric so that the amount of deposition is formed preferentially more on the masking material. It is preferred such a process is aided  
30 by the line-of-sight of the location to the deposition source as well as by the selective nature of the chosen CVD process. In other words, the deposition chemistry be chosen in such a way that a coating is formed preferentially on the masking materials due to differences in the chemical inertness of the materials. As can be seen in FIG. 4B a thicker protective layer 412 is formed on the top of the photoresist mask 404 than on the oxide surface on the bottom of

the photoresist mask and on the sidewalls of the photoresist mask. In the preferred embodiment, the deposition is done in-situ in an etch chamber using a chemical vapor deposition (CVD) process, which also deposits a thin protective layer on the sidewall of the photoresist. Preferably the deposition uses some ion energy to allow for selectivity of such deposition.

In other embodiments, the processing conditions may be changed to vary the thickness and spatial distribution of the protective layer. For example, it may be desirable to form a thicker coating on the sidewall of the etching structures as the etching proceeds deeper in order to protect the etching structure from further distortion by the subsequent etching. A variation of processing conditions may provide for this. Since passivation and etching are separate steps, the process conditions for passivation may be optimized for this result without interfering with the etching process.

During the deposition, the fluorine-to-carbon ratio of the deposition gas is not greater than 2:1. Examples of deposition chemistries that may be used for CVD may be, but are not limited to,  $\text{CH}_3\text{F}$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{C}_2\text{H}_5\text{F}$ ,  $\text{C}_3\text{H}_7\text{F}$ ,  $\text{C}_2\text{H}_3\text{F}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_3\text{H}_8$ , and  $\text{SiH}_4$ ,  $\text{Si}(\text{CH}_3)_4$ ,  $\text{Si}(\text{C}_2\text{H}_5)_4$ . It is preferred that these chemicals are halogen free or have a halogen to carbon ratio of no greater than 2:1. Without being limited by theory, it is believed that the carbon based chemistry forms a thin etch resistant amorphous carbon layer. The silane  $\text{SiH}_4$  would be used to form an amorphous silicon layer (or polyamorphous silicon) over the photoresist. In addition, the protective layer may have been modified with the presence of some F and H components. The presence of other elements, such as F, may be used to yield selective activity on different material surfaces such that deposition occurs preferentially on one but not the other materials, such as on the photoresist mask materials but not on  $\text{SiO}_2$  layer, under appropriate ion bombardment. The thinness and etch resistance provides a protection sufficient to resist photoresist etch or damage and thin enough to allow etching of the desired feature shape. Other methods, such as sputtering, may be used to deposit a protective layer on the photoresist mask before etching. The passivation step is an independent step in the etch process which may include different combinations of deposition gases for different etching applications of different materials, where the deposition provides a protective coating around the etching features including the masking features using possible multistep gas switching sequences. To accomplish this step, the controller 535 may cause the first valve 537 to allow a deposition gas from the deposition gas source 512 into the process chamber 500, while causing the second valve 539 from preventing etching gas from the etchant gas source 514 from entering the process chamber. The controller 535 may also

control the power supplied by the first and second RF sources 544, 548 and the exhaust pump 520. The controller may also be used to control the wafer pressure, backside He cooling pressure, the bias on the substrate, and various temperatures.

Table I is a table of some of the parameters that may be used in a passivation and etching step in the preferred embodiment of the invention.

Table I

	Preferred Range	More Preferred Range	Most Preferred Range
Bias Voltage	>50 volts	> 100 volts	> 300 volts
Bias Energy	>50 eV	> 100 eV	> 300 eV

The bias may be provided by placing a constant voltage between an upper electrode above the substrate and a lower electrode below the substrate. In the preferred embodiment, an electrical negativity can be formed on the substrate holding the wafer materials (thereby applying a bias to the wafer) by applying a radio frequency (RF) voltage supplied by an RF power generator. This has the effect of drawing the positively charged particles towards the electrically biased substrate at an energy determined by the electrical negativity controlled by the amplitude of the RF voltage. It is, therefore, possible to supply and vary the ion bombardment energy by controlling the RF power (and hence the RF voltage) applied to the substrate holder.

Next, the oxide layer 408 is etched through the photoresist mask 404, to form a feature 416, as shown in FIG. 4C. Etching applications may include, but are not limited to, a dielectric contact etch (high aspect ratio contact (HARC) or damascene), conductor trench etch (shallow or deep), self-aligned contact etch, gate mask open etch, contact etch, via dielectric etch, dual-damascene via etch, dual damascene trench etch, conductor gate etch, conductor deep trench etch, conductor shallow trench isolation etch, and hardmask opening. Preferably, the etch uses a high ion energy to provide a directional etch. The etch may remove some of the protective layer 412, as shown. All of the protective layer on some of the surfaces may be removed. In this example, the protective layer forming the side wall on the photoresist 404 has been removed. Other parts of the protective layer may only be partially removed. In this example, only part of the protective layer 412 on the top surface of the photoresist 404 has been removed. In other embodiments, other parts of the protective layer may be partially etched way or completely etched away. To accomplish this step, the



controller 535 may cause the first valve 537 to stop the flow of the deposition gas from the deposition gas source 512 into the process chamber 500, while causing the second valve 539 to allow the etching gas from the etchant gas source 514 to flow into the process chamber. The controller 535 may change the power supplied by the first and second RF sources 544, 548 and change the setting of the exhaust pump 520 to accommodate the etching. The controller may also be used to change the wafer pressure, backside pressure, and various temperatures to accommodate the etching process. Since this etch step uses high energy ions to provide a directional etch, a polymer former gas is provided during the etch. The polymer former gases may be, for example, hydrocarbons, fluorocarbons, and hydrofluorocarbons, such as C<sub>4</sub>F<sub>6</sub>, C<sub>4</sub>F<sub>8</sub>, CH<sub>3</sub>F, CH<sub>2</sub>F<sub>2</sub>, CH<sub>4</sub>, C<sub>3</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, and CHF<sub>3</sub>. These polymer former gases would form a polymer layer that is constantly added and etched away during the etch.

Table II is a table of some of the parameters that may be used in an etching process in the preferred embodiment of the invention.

Table II

	Preferred Range	More Preferred Range	Most Preferred Range
Bias Voltage	>200 volts	> 300 volts	> 400 volts
Bias Energy	>200 eV	> 300 eV	> 400 eV

After the contact hole is at least partially etched, a determination is made on whether to etch more (step 316). This may be done by a set recipe or by taking a measurement. If more etching is desired, then the process cycles back to step 308, where an additional protective layer 418 is deposited on the photoresist mask, as shown in FIG. 4D. In this example, the remaining part of the old protective layer becomes part of the new protective layer 418. In this step, again the controller 535 opens the first control valve 537 to provide deposition gas and closes the second control valve 539 to stop the flow of the etching gas. The controller 535 may also change other parameters to accommodate the deposition.

The contact hole is then further etched through the photoresist mask (step 312), providing a deeper contact hole 416, as shown in FIG. 4E. In this step, again the controller 535 closes the first control valve 537 to stop the deposition gas and opens the second control valve 539 to allow the flow of the etching gas. The controller 535 may also change other parameters to accommodate the etching.

Preferably, this cycle or loop of providing alternating deposition and etching steps is repeated more than once. Preferably, this cycle is repeated more than three times. Preferably, this cycle is repeated at least five times. This cycle may be repeated dozens of times. It may be desirable to repeat this cycle 100 times.

5 Preferably, in at least the last cycle, the etching step completely etches away the protective layer, as shown in FIG. 4E. When no further etching is desired, the photoresist mask is stripped (step 320) to yield the oxide layer 408 with a contact hole 416, as shown in FIG. 4F. The photoresist mask may be stripped in the process chamber 500 or after removal from the process chamber 500.

10 In other embodiments, an etch step may be added before step 308 for depositing a protective layer on the photoresist mask.

Preferably, the etching and the deposition of the protective layer are done in the same chamber, but may be done in different chambers. An Exelan, DFC 2300 made by LAM Research Corp. of Fremont, California may be adapted to perform both the deposition and  
15 etch steps. Since the deposition and etch are done in the same chamber, cycling between the deposition and etch may be done quickly.

Examples of materials for the photoresist mask may include, but are not limited to the newer generation of photoresist, such as, deep UV photoresist, 193 nm photoresist, 157 nm photoresist, EUV photoresist, e-beam photoresist, and x-ray photoresist. The  
20 older generation of photoresist polymer materials are designed to contained unsaturated C-C bonds, such as the C-C double bond and even C-C triple bonds to provide the required high etching resistance, namely, chemical inertness to the etching gas mixture. These bonds are strong and require a high activation energy to break and therefore, at relatively low ion energies, the older generation photoresist can show  
25 remarkably low etching rate to the etching gas mixture. The newer generation of photoresist, including 193nm and 157nm, does not contain these unsaturated bonds because these unsaturated bonds absorbs at the lithography exposure wavelength, leading to much reduced photoresist etching resistance. By providing a protective coating on the photoresist during the etching phase, using an etching mixture  
30 containing at least one passivation gas, the etching resistance of the photoresist is much improved, even at high ion bombardment energy. The high ion bombardment energies at which the invention may improve etching resistance of the photo resist may be 50-2,000 eV. More preferably the ion bombardment energy may be 200-1,500 eV. Most preferably the ion bombardment energy is 500-1,000 eV.

Via etching example

A specific example of the invention, for etching a SiO<sub>2</sub> layer with a 193 photoresist mask and a bottom antireflective coating (BARC) between the SiO<sub>2</sub> layer and the photoresist mask, uses an Exelan DFC 2300 for the process chamber 500. In the process chamber 500, a BARC etch is performed. The BARC etch has a pressure of 110 millitorr, which may be set by the confinement rings 502, the exhaust pump 520 and the flow rate through the gas inlet 543. The power applied at 27 MHz is 1200 watts, and no power at 2 MHz through the electrodes 504, 508. The etch chemistry is 700 sccm of Argon, 60 sccm of CF<sub>4</sub>, and 12 sccm of O<sub>2</sub>. The upper electrode 504 is placed at a temperature of 180° C. The chuck formed by the lower electrode 508 is placed at a temperature of 10° C. A backside inner zone chuck pressure of helium is placed at 15 torr. A backside outer zone chuck pressure is placed at 15 torr. In this example, the BARC etch is maintained for 50 seconds. The controller 535 controls these parameters. The additional gas source 516 may be used to provide gases for the BARC etch. The additional gas source 516 may represent more than one gas source. The third valve 541 may represent more than one valve, so that the additional gases may be independently controlled by the controller 535. For an Exelan DFC 2300, a back side pressure of helium is used to cool the chuck. The Exelan DFC 2300 allows for an inner backside pressure, which is closer to the center of the chuck and an outer backside pressure which is closer to the outer edge of the chuck. The controller 535 is able to control these pressures.

A deposition of the protective layer is performed in the Exelan DFC 2300 at a pressure of 50 millitorr, with 800 watts applied at 27 MHz and 400 watts applied at 2 MHz. The deposition chemistry is 500 sccm of Argon and 50 sccm of CH<sub>3</sub>F. The upper electrode is placed at a temperature of 180° C. The chuck is placed at a temperature of 10° C. The backside inner zone chuck pressure of helium is placed at 30 torr. The backside outer zone chuck pressure is placed at 12 torr. In this example, the deposition gas source 512 would provide the CH<sub>3</sub>F, which is not provided during the etching. The argon may be provided from the additional gas source 516, since argon is provided during both the deposition and etching. The controller 535 would open the first valve 537 and close the second valve 539. The controller would also control the flow of argon from the additional gas source. The controller 535 would control the power and other parameters as specified above.

An etching of the SiO<sub>2</sub> layer is performed in the Exelan DFC 2300 at a pressure of 40 millitorr, with 2500 watts applied at 27 MHz and 3500 watts applied at 2 MHz. The etch chemistry is 400 sccm of Argon, 36 sccm of C<sub>4</sub>F<sub>6</sub>, and 30 sccm of O<sub>2</sub>. The C<sub>4</sub>F<sub>6</sub> would be a polymer former gas, which provides polymerization during the etching. The O<sub>2</sub> would be the

etching enabler gas. Although the fluorine from  $C_4F_6$  is used in etching, the fluorine in this example requires the presence of oxygen to enable etching. The upper electrode is placed at a temperature of  $180^\circ\text{C}$ . A chuck is placed at a temperature of  $10^\circ\text{C}$ . A backside inner zone chuck pressure of helium is placed at 30 torr. A backside outer zone chuck pressure is placed at 12 torr. In this example, the etchant gas source 514 would provide the  $C_4F_6$  and  $O_2$ , which is not provided during the deposition, although  $C_4F_6$  without oxygen may be used during deposition. The controller 535 would close the first valve 537 and open the second valve 539. The controller would also control the flow of argon from the additional gas source. The controller 535 would control the power and other parameters as specified above.

In this example, first the BARC etch is performed for 50 seconds. Next, the deposition of the protective layer (step 308) is performed for 10 seconds. Next, the contact hole is etched for 25 seconds (step 312). Then the deposition of the protective layer is performed for 10 seconds (step 308). The etch of the feature for 25 seconds (step 312) and the deposition of the protective layer for 10 seconds (step 308) is repeated four times. A final etch of the feature is performed for 80 seconds (step 312). The cycle is completed (step 316) and the photoresist is stripped (step 320). Therefore, in this example, the deposition (step 308) and etch (step 312) cycle is performed for 5 cycles.

Another notation for this same sequence can be written as:

50 sec. BARC etch + 10 sec. deposition +  $4 \times (25 \text{ sec. etch} + 10 \text{ sec. deposition}) + 80 \text{ sec. etch}$ .

In this example, the protective layer is preferentially formed on the mask and sidewalls of the feature, so that the protective layer is thicker on the mask and sidewalls of the feature than on the bottom of the feature or that no protective layer is formed at all at the bottom of the feature.

Different conditions may be used between cycles to more specifically tailor the conditions to the process. Additional processes may be added to each cycle. Although in this example the process chamber is an Exelan DFC 2300, other modified etching systems may be used.

FIG. 6 is a photomicrograph of a  $SiO_2$  layer 604, which was masked with a 193 photoresist mask to form high aspect ratio contact (HARC) etches 608, using the inventive deposition of a protective layer and etch process. FIG. 7 is a photomicrograph of a  $SiO_2$  layer 704, which was masked with a 193 photoresist mask to form high aspect ratio contact (HARC) etches 708, without using the inventive deposition of a protective layer and etch process. As can be seen by comparing FIG. 6 and FIG. 7, the inventive process of deposition and etching provides the desired pattern transfer from the photoresist mask (the original mask

patterns are arrays of circular holes) in that the contacts are more circular. On the other hand, the prior art method of an etch without the deposition of a protective layer for the photoresist causes a distortion of the original patterns, which is apparent in the dielectric layer as shown by the more irregular shape of the contact holes and which is not acceptable. The protective  
5 layer on the sidewalls of the photoresist and feature may also prevent striation, that is found in some etch processes.

The invention provides a more cost effective process than the use of a stacked mask, since the production of a stacked photoresist mask is more complicated. The invention may also provide better etch results at less expense than a stacked mask process.

10 The layer to be etched may be a dielectric layer (such as silicon oxide), a conductive layer (such as metal and silicon or other type of semiconductors), or a hardmask layer (such as silicon nitride and silicon oxynitride). For etching a conductor layer, halogens, such as chlorine, fluorine, or bromine, may be used in the etching step, where the deposition may contain chemicals used to deposit a C-rich thin film or a thin film containing Si.

15 In the preferred embodiment of the invention, it is desirable that some of the components of the deposition gas are not mixed with components of the etch gas, since some mixing decreases the efficiency of having a separate deposition and etch process. As a result, the controller should time the gas flows so that one gas is depleted before another gas is added.

20 In the preferred embodiment, the etchant gas from the etching gas source is not provided to the plasma processing chamber during the deposition step and the deposition gas from the deposition gas source is not provided to the plasma processing chamber during the etching step. This may be done by not providing a component of the etching gas or deposition gas. For example, oxygen or an oxygen containing gas is a key etching component to an  
25 etching gas. Even though  $C_4F_6$  is also used in the etchant gas, etching cannot be accomplished by  $C_4F_6$  without oxygen in this example. So not providing oxygen or an oxygen containing gas during the deposition step is a method of not providing the etching gas during the deposition step, even if  $C_4F_6$  is provided during deposition. It is also preferred that the deposition process is a non-etching or negligently etching at most (comprising less than 10%  
30 of the layer to be etched) for forming the protective coating. Such a deposition process may be, but is not limited to, CVD deposition or sputtering, since CVD and sputtering are not used for etching. If the deposition gas is the same as the polymer former in the etch step, then the deposition gas may be provided during the etch step. In such a case, one difference between the deposition step and the etch step is that an etching component of the etch gas is present

only during the etch step. In addition, bias power during the etch step may be higher to provide the directional etching.

Providing a separate deposition step and the presence of the polymer former to provide polymerization during the etch step allows the use of higher energy etching ions for higher etching rate and better anisotropic etching.

By keeping passivation gases in an etching mixture, it is possible to use higher ion energies without unacceptable erosion and damage of the etching mask. Additionally, anisotropic etching can be achieved during the duration of the etching step. By using separate passivation steps, profile and mask protection can be optimized by choosing, for example, a passivation chemical mixture that forms a harder and more durable coating than produced by an etching mixture, since the interaction of etching and retardation gases in the discharge can degrade the quality of the coating. Additionally, the passivation chemistry conditions, such as pressure and concentration, may be tailored to optimize the properties of the passivation coating such as the composition, thickness.

Therefore, by having independent passivation and etch-passivation steps processing conditions, such as temperature, power, pressure, ion energy, and processing gases, may be independently controlled varied to provide optimal conditions for each step to provide an optimized coating and an optimized etch.

Other inert gases instead of argon may be used as carrier gases during both the etching and deposition. An example of another inert gas would be neon.

In an embodiment of the invention, the chamber wall areas, which may contact the plasma (a mixture of chemicals and charged particles sustained by the electrical discharge), are made to be as small as possible and to be maintained at elevated temperatures. The object of this is to minimize the total deposition on the chamber wall areas so as to avoid the so-called "memory" effect, by which the chemical elements contained in the coating of the chamber wall areas formed in one processing step can be released to interfere with the subsequent steps.

It may also be desirable that the gas travel time from the precursor source to the processing chamber is made to be very short. The gas flow stability time, denoting the time to establish a constant desired flow and the time to establish complete absence of the said gas at the processing chamber, is made to be very short so that the transition from one stable gas mixture composition to the next can be made to be very fast. The

object of this is to avoid inter-mixing of chemicals between two different steps, which can degrade the performance.

It may also be desirable that the electrical system and the control network controlling the conversion of the electrical power into an electrical discharge reacts  
5 very fast with respect to the changes of the discharge conditions and power requirements. Furthermore, it may be desirable to be able to quickly change and stabilize other external conditions of the processing chamber, such as the pressure of the gas mixture and the temperature of the wafer substrate. Since the two different steps may be repeated a large number of times process conditions to accommodate each step  
10 must be changed several times. Allowing such process conditions to be changed quickly allows for a faster cycling time and allows the process conditions to be varied significantly between steps to optimize each step individually. Therefore, it may also be desirable to have a central computerized system that is able to control and synchronize the rapid changing of the processing conditions. The computer is used to  
15 send commands for the required changes and synchronize with a pre-determined time delays of various devices providing the plurality of condition changes in the processing chamber.

The deposition step may comprise a series of different coating steps. The etching step may comprise a series of different etching steps.

20

#### Trench Etch Example

FIG. 13 is a high level flow chart for an example for forming a dual damascene feature using a via first scheme. First a plurality of vias are formed (step 1304). The vias may be formed using the method described in the previous example. FIG. 14A is  
25 a cross-sectional view of part of a substrate 1410 over which a trench pattern mask 1428 has been formed. A first contact 1404 and a second contact 1406 may be placed in a low-k dielectric layer 1408 over the substrate 1410. A dielectric barrier layer 1412, typically, but not limited to silicon nitride or silicon carbide, may be placed over the first and second contacts 1404, 1406 to prevent the copper diffusion. A low-k  
30 dielectric layer 1420 was placed over the barrier layer 1412. First 1440 and second 1444 vias have been etched into the low-k dielectric layer 1420. Partial plugs 1448 may be formed at the bottom of the vias (step 1308). This is an optional step. In some embodiments, this step of forming a partial plug would be omitted. A trench patterned mask 1428 is formed over the substrate (step 1312).

The low-k dielectric layer 1420 is subjected to a trench etch cycle 1314. The trench etch cycle 1314 comprises the steps of depositing a protective layer on the sidewalls of the via with a plasma deposition (step 1316) and etching through the mask (step 1312). The cycle is repeated until the end of the etch (step 1324). In a preferred embodiment, the trench etch cycle is repeated at least one time. More preferably, the trench etch cycle is repeated at least three times. Most preferably, the trench etch cycle is repeated at least five times. It is believed that the greater number of cycles allows for thinner sidewalls to be applied with each cycle, allowing for a reduction in fencing and reduced faceting. FIG. 14B is a cross-sectional view of part of the substrate 1410 after the protective layer 1452 has been deposited. Preferably, the deposition of the protective layer is an isotropic line-of-sight plasma deposition, which in this embodiment forms a thicker layer on the top surface of the mask and a thinner layer on the sidewalls of the vias. Most preferably, the deposition is of a surface reaction type, in which case the deposited protective layer is conformal, meaning to possess equal thickness on the top as well as the sidewall surfaces. Preferably, the deposition process also contains such directional removal mechanism, such as ion assisted etching or sputtering, in such a manner that the net effect of applying the deposition process is to yield a protective coating on the vertical sidewall surface with little or no deposition on the horizontal surface that may impede progression of the trench etching process. It is therefore preferred that the deposition process also is of sufficiently high ion energy so as to effect a selective sidewall protection, meaning that a protective coating selectively forms only on the vertical profile sidewall but not the horizontal etching front surfaces of the dielectric layer to be etched. A protective coating can be formed on the horizontal top surfaces of the mask pattern since the chemistry is carefully selected in such a way that it is reactive towards the dielectric layer but not reactive towards the mask layer. FIG. 14C is a cross-sectional view of part of the substrate 1410 after the step of etching the trench through the mask (step 1320). Some or all of the via sidewall is etched away. In the preferred embodiment, the etching is a high ion energy directional anisotropic etch.

After the trench is partially etched, if the etching is to continue (step 1324) the process cycles back up to step 1316 where another protective layer 1460 is deposited, which again forms protective sidewalls in the vias, as shown in FIG. 14D. More etching of the trench is performed (step 1320) to further deepen the trench 1456, as shown in FIG. 14 E. The cycle is continued until the trench is etched to the desired



depth (step 1324). Then the remaining protective layer and mask is stripped (step 1328).

This embodiment provides sidewall protection to prevent faceting. The need for a high plug to prevent faceting may be eliminated. A shorter plug may be used to prevent the opening of the barrier layer. However, some embodiments may eliminate all plugs.

#### Recipe

In a specific example of the invention, a Coral<sup>TM</sup> layer is etched to form a dual damascene feature using a via first method. Vias are first etched into the Coral (step 1304). In this example, no partial plug is formed. A photoresist trench pattern mask is formed over the Coral layer (step 1312). An antireflective layer or other layers may be placed between the coral layer and the photoresist mask. In such a case, various etch steps may be added to open such intermediate layers.

A deposition of the protective layer on sidewalls of the via (step 1316) is performed in the Exelan DFC 2300 at a pressure of 80 millitorr, with 400 watts applied at 27 MHz and 0 watts applied at 2 MHz. The deposition chemistry is 600 sccm of Argon, 80 sccm H<sub>2</sub>, and 60 sccm of CF<sub>4</sub>. The upper electrode is placed at a temperature of 25° C. The chuck is placed at a temperature of 20° C. The backside inner zone chuck pressure of helium is placed at 15 torr. The backside outer zone chuck pressure is placed at 15 torr. This step is carried out for 45 seconds.

An etching of trenches into the Coral<sup>TM</sup> layer is performed in the Exelan DFC 2300 at a pressure of 80 millitorr, with 800 watts applied at 27 MHz and 0 watts applied at 2 MHz. The etch chemistry is 200 sccm of Argon, 60 sccm of CF<sub>4</sub>, 20 sccm CHF<sub>3</sub>, and 10 sccm of O<sub>2</sub>. The CF<sub>4</sub> would be a polymer former gas, which provides polymerization during the etching. The O<sub>2</sub> would be the etching enabler gas. Although the fluorine from CF<sub>4</sub> is used in etching, the fluorine in this example requires the presence of oxygen to enable etching. The upper electrode is placed at a temperature of 25° C. A chuck is placed at a temperature of 20° C. A backside inner zone chuck pressure of helium is placed at 15 torr. A backside outer zone chuck pressure is placed at 15 torr.

The trench etching gas should contain at least one of the polymer former gas component as well as at least one etching gas component. The polymer former gas is needed to provide sidewall protection on the trench sidewall surface to effect a vertical trench profile in an anisotropic etching manner. It should be noted that the trench vertical surfaces are being continuously opened up during the trench etching duration hence needs to be protected during

the trench etching duration, while the via vertical surfaces are opened before the trench etching is commenced, since trench and via vertical sidewalls are quite different. Medium to high ion energies are also preferred to benefit such properties as trench profile, mask and underlayer selectivities. In the etching example, the 800w 27MHz RF power provides > 200  
5 ev of ion bombardment energy. Even higher ion energy is possible depending upon its effect on such trench etching properties as micro-trenching, aspect ratio dependency, etc.

The deposition of the protective layer (step 1316) is performed for 45 seconds. Next, the trench is etched for 30 seconds (step 1320). The deposition of the protective layer (step 1316) and the etching of the trench (step 308) may be repeated a number of times, which  
10 provides a trench etch of 3300 Å.

FIG. 15A is a photomicrograph of a cross-sectional view of a dual damascene feature that has been etched according to the example. FIG. 15B is a top and side perspective view of the dual damascene feature. Vias 1504 are etched into the Coral layer 1508. A trench 1512 is also etched into the Coral layer. Since this example did not use a partial plug, no plug is in  
15 the vias, so that an additional step of removing the plug is not needed. The via and trench are well formed, although a small amount of faceting 1516 may be seen. The micrograph also shows that fencing in this example has been either significantly reduced or eliminated.

FIG.'S 8A and 8B illustrate a computer system 800, which is suitable for using as the controller 535. FIG. 8A shows one possible physical form of a computer system  
20 that may be used for the controller 535. Of course, the computer system may have many physical forms ranging from an integrated circuit, a printed circuit board, and a small handheld device up to a huge super computer. Computer system 800 includes a monitor 802, a display 804, a housing 806, a disk drive 808, a keyboard 810, and a mouse 812. Disk 814 is a computer-readable medium used to transfer data to and  
25 from computer system 800.

FIG. 8B is an example of a block diagram for computer system 800. Attached to system bus 820 are a wide variety of subsystems. Processor(s) 822 (also referred to as central processing units or CPUs) are coupled to storage devices, including memory  
824. Memory 824 includes random access memory (RAM) and read-only memory  
30 (ROM). As is well known in the art, ROM acts to transfer data and instructions uni-directionally to the CPU and RAM is used typically to transfer data and instructions in a bi-directional manner. Both of these types of memories may include any suitable type of the computer-readable media described below. A fixed disk 826 is also coupled bi-directionally to CPU 822; it provides additional data storage capacity and

may also include any of the computer-readable media described below. Fixed disk 826 may be used to store programs, data, and the like and is typically a secondary storage medium (such as a hard disk) that is slower than primary storage. It will be appreciated that the information retained within fixed disk 826 may, in appropriate cases, be incorporated in standard fashion as virtual memory in memory 824.

Removable disk 814 may take the form of any of the computer-readable media described below.

CPU 822 may be also coupled to a variety of input/output devices, such as display 804, keyboard 810, mouse 812 and speakers 830. In general, an input/output device may be any of: video displays, track balls, mice, keyboards, microphones, touch-sensitive displays, transducer card readers, magnetic or paper tape readers, tablets, styluses, voice or handwriting recognizers, biometrics readers, or other computers. CPU 822 optionally may be coupled to another computer or telecommunications network using network interface 840. With such a network interface, it is contemplated that the CPU might receive information from the network, or might output information to the network in the course of performing the above-described method steps. Furthermore, method embodiments of the present invention may execute solely upon CPU 822 or may execute over a network such as the Internet in conjunction with a remote CPU that shares a portion of the processing.

In addition, embodiments of the present invention further relate to computer storage products with a computer-readable medium that have computer code thereon for performing various computer-implemented operations. The media and computer code may be those specially designed and constructed for the purposes of the present invention, or they may be of the kind well known and available to those having skill in the computer software arts. Examples of computer-readable media include, but are not limited to: magnetic media such as hard disks, floppy disks, and magnetic tape; optical media such as CD-ROMs and holographic devices; magneto-optical media such as floptical disks; and hardware devices that are specially configured to store and execute program code, such as application-specific integrated circuits (ASICs), programmable logic devices (PLDs) and ROM and RAM devices. Examples of computer code include machine code, such as produced by a compiler, and files containing higher level code that are executed by a computer using an interpreter. Computer readable media may also be computer code transmitted by a computer data signal embodied in a

carrier wave and representing a sequence of instructions that are executable by a processor.

While this invention has been described in terms of several preferred embodiments, there are alterations, permutations, and substitute equivalents, which  
5 fall within the scope of this invention. It should also be noted that there are many alternative ways of implementing the methods and apparatuses of the present invention. It is therefore intended that the following appended claims be interpreted as including all such alterations, permutations, and substitute equivalents as fall within the true spirit and scope of the present invention.

10

**CLAIMS**

What is claimed is:

1. A method for etching a feature in a layer through an etching mask comprising:  
forming a protective coating on exposed surfaces of the etching mask and  
5 vertical sidewalls of the feature with a passivation gas mixture; and  
etching the feature through the etching mask with reactive etching mixtures  
containing at least one etching chemical and at least one passivation chemical.
2. The method, as recited in claim 1, wherein the etching comprises providing an  
10 ion bombardment energy of greater than 200 electron volts to the substrate.
3. The method, as recited in claim 2, wherein the etching chemical contains a  
polymer former and an etch enabler.
- 15 4. The method, as recited in claim 3, wherein the passivation and etching are  
performed in a common plasma processing chamber.
5. The method, as recited in claim 4, wherein the deposition uses a non-  
directional deposition and the etching step uses a directional etching.  
20 6. The method, as recited in claim 5, wherein the passivation is a non-etching or a  
negligibly etching deposition.
- 7 The method, as recited in claim 6, wherein the deposition process is selected  
25 from at least one of chemical vapor deposition and sputtering.
8. The method, as recited in claim 7, wherein the depositing and etching are  
performed in a sequentially alternating fashion at least four times.
- 30 9. The method, as recited in claim 1, wherein the etching mask is a photoresist  
mask 193 nm or below generation.
- 10 The method, as recited in claim 1, wherein the protective coating is formed  
preferentially on the exposed areas of the etching mask and the vertical sidewalls of

the features.

11. The method, as recited in claim 10, wherein at least one passivation chemical releases a polymerizing agent that is more chemically active to the layer than the mask materials.

12. The method, as recited in claim 10, wherein directional energetic ions are used to preferentially prevent deposition from accumulating at the horizontal surfaces of the layer during the step of the formation of protective coating by activating a removal mechanism of the coating on selectively the surface of the layer.

13 The method, as recited in claim 11, wherein at least one passivation chemical is a hydrofluorocarbon with F:C ratio of less than 2:1.

14. The method, as recited in claim 11, wherein at least one of the passivation chemical is one of the  $\text{CH}_3\text{F}$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{C}_2\text{H}_5\text{F}$ ,  $\text{C}_2\text{H}_4\text{F}_2$ ,  $\text{C}_3\text{H}_7\text{F}$ ,  $\text{C}_3\text{H}_6\text{F}_2$ ,  $\text{C}_2\text{H}_3\text{F}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_2\text{H}_2$ .

15. The method, as recited in claim 11, wherein the at least one passivation chemical is a mixture of Ar and  $\text{CH}_3\text{F}$ .

16. The method, as recited in claim 12, wherein the ion energy provided in the passivation step is greater than 100 electron volts.

17. The method, as recited in claim 1, wherein at least one of the etching chemicals is  $\text{C}_4\text{F}_6$ .

18. The method as recited in claim 1, wherein at least one of the RF frequencies used for the discharge is one of the 2MHz, 27MHz and 60MHz.

19. The method, as recited in claim 1, wherein the RF discharge frequencies consist of a combination a lower frequency in the range of 400KHz to 13.56MHz and another higher frequency in the range of 27MH to 120MHz.

20. An apparatus for etching a layer under an etch mask, wherein the layer is supported by a substrate, comprising:

a plasma processing chamber, comprising:

a chamber wall forming a plasma processing chamber enclosure;

5 a substrate support for supporting a substrate within the plasma processing chamber enclosure;

a pressure regulator for regulating the pressure in the plasma processing chamber enclosure;

10 at least one electrode for providing power to the plasma processing chamber enclosure for sustaining a plasma;

a gas inlet for providing gas into the plasma processing chamber enclosure; and

a gas outlet for exhausting gas from the plasma processing chamber enclosure;

15 a deposition gas source;

an etchant gas source;

a first control valve in fluid connection between the gas inlet of the plasma processing chamber and the deposition gas source;

20 a second control valve in fluid connection between the gas inlet of the plasma processing chamber and the etchant gas source;

a controller controllably connected to the first control valve, the second control valve, and the at least one electrode, comprising:

at least one processor; and

computer readable media, comprising:

25 computer readable code for opening the first control valve for at least one deposition step to provide a deposition gas from the deposition gas source to the plasma processing chamber enclosure;

30 computer readable code for closing the second control valve for the at least one deposition step to prevent etching gas from the etchant gas source from entering the plasma processing chamber enclosure;

computer readable code for opening the second control valve for at least one etching step to provide an etching gas from the etchant gas source to the plasma processing chamber; and

computer readable code energizing the at least one electrode to

provide a bias of greater than 250 volts on the substrate for the at least one etching step.

21. The apparatus, as recited in claim 20, further comprising:

5 a passivation gas source; and

a third control valve in fluid connection between the gas inlet of the plasma processing chamber and the passivation gas source,

wherein the computer readable media further comprises computer readable code for opening a third control valve for the at least one etching step to provide  
10 passivation gas from the passivation gas source to the plasma processing chamber.

22. The apparatus, as recited in claim 19, wherein the computer readable media further comprises computer readable code for performing the at least one deposition step and at least one etching step in an alternating fashion for a plurality of times.

15 23. A method for forming a dual damascene feature, comprising:

forming vias in an etch layer;

providing a trench patterned mask over the etch layer;

etching a trench, wherein the etching the trench comprises a cycle of:

20 forming protective sidewalls over the sidewalls of the vias; and

etching a trench through the trench patterned mask; and

stripping the mask. etching steps, including the stripping the mask

24. The method as recited in claim 23, wherein the trench cycle is repeated at least  
25 three times.

25. The method as recited in claim 23, wherein the trench etch cycle is repeated at least five times.

30 26. The method, as recited in claim 25, wherein the passivation and etching are performed in a common plasma processing chamber.

27. The method, as recited in claim 26, wherein the deposition uses a non-directional deposition and the etching step uses a directional etching.



28. The method, as recited in claim 27, wherein the wafer is bombarded by energetic ions with ionic energy greater than 100 ev during the deposition step.

5 29. The method, as recited in claim 27, wherein the passivation is a non-etching or a negligibly etching deposition.

30. The method, as recited in claim 27, wherein the deposition uses a gas mixture containing at least one of H<sub>2</sub>, CH<sub>3</sub>F, CH<sub>2</sub>F<sub>2</sub>, CHF<sub>3</sub>, C<sub>4</sub>F<sub>6</sub>, C<sub>4</sub>F<sub>8</sub> as the polymer  
10 former and at least one of CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, and NF<sub>3</sub> as the etching gas.

31. The method, as recited in claim 27, wherein the deposition step uses a mixture containing CF<sub>4</sub> and H<sub>2</sub>.

15 32. The method as recited in claim 31, wherein the CF<sub>4</sub> to H<sub>2</sub> gas flow ratio is in the range of 0.6:1 to 1.4:1 by volume flow rate.

33. The method, as recited in claim 29, wherein the deposition process is selected from at least one of chemical vapor deposition and sputtering.

20

34. The method, as recited in claim 23, wherein the etch layer is a low-k dielectric material.

35. The method, as recited in claim 23, wherein the via holes are not filled with a  
25 sacrificial filler material prior to the start of the trench plasma etching process.

36. The method, as recited in claim 33, wherein the via holes are filled with a filler material to no more than 50% of the via hole height prior to the start of the trench plasma etching process.

30

37. A semiconductor formed by the method of claim 23.

38. An apparatus for performing the method of claim 23.

39. An apparatus for etching a layer under an etch mask, wherein the layer is supported by a substrate, comprising:

a plasma processing chamber, comprising:

a chamber wall forming a plasma processing chamber enclosure;

5 a substrate support for supporting a substrate within the plasma processing chamber enclosure;

a pressure regulator for regulating the pressure in the plasma processing chamber enclosure;

10 at least one electrode for providing power to the plasma processing chamber enclosure for sustaining a plasma;

a gas inlet for providing gas into the plasma processing chamber enclosure; and

a gas outlet for exhausting gas from the plasma processing chamber enclosure;

15 a deposition gas source;

an etchant gas source;

a first control valve in fluid connection between the gas inlet of the plasma processing chamber and the deposition gas source;

20 a second control valve in fluid connection between the gas inlet of the plasma processing chamber and the etchant gas source;

a controller controllably connected to the first control valve, the second control valve, and the at least one electrode, comprising:

at least one processor; and

computer readable media, comprising:

25 computer readable code for opening the first control valve for at least one deposition step to provide a deposition gas from the deposition gas source to the plasma processing chamber enclosure;

30 computer readable code for closing the second control valve for the at least one deposition step to prevent etching gas from the etchant gas source from entering the plasma processing chamber enclosure; and

computer readable code for opening the second control valve for at least one etching step to provide an etching gas from the etchant gas source to the plasma processing chamber.

40. The apparatus, as recited in claim 39, wherein the computer readable media further comprises computer readable code for performing the at least one deposition step and at least one etching step in an alternating fashion for a plurality of times.
- 5 41. The apparatus, as recited in claim 39, wherein the etchant gas source comprises an etching gas component source and a polymer former gas component.

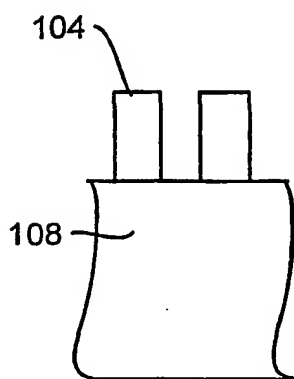


FIG. 1A  
(PRIOR ART)

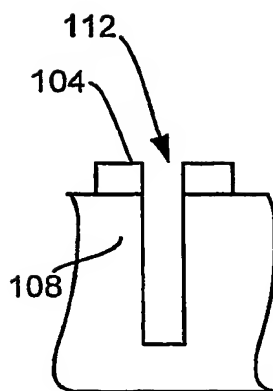


FIG. 1B  
(PRIOR ART)

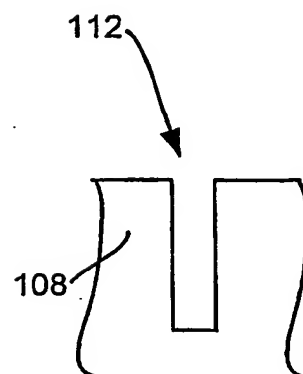


FIG. 1C  
(PRIOR ART)

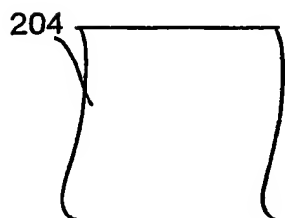


FIG. 2A  
(PRIOR ART)

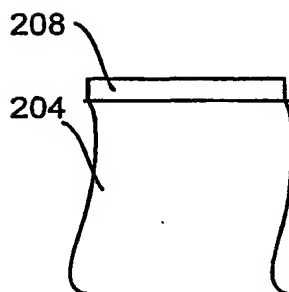


FIG. 2B  
(PRIOR ART)

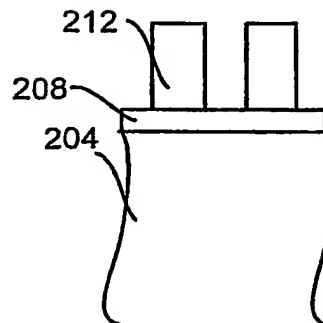


FIG. 2C  
(PRIOR ART)

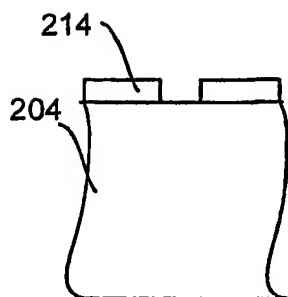


FIG. 2D  
(PRIOR ART)

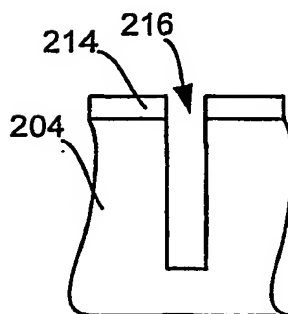


FIG. 2E  
(PRIOR ART)

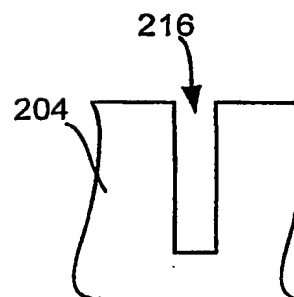


FIG. 2F  
(PRIOR ART)

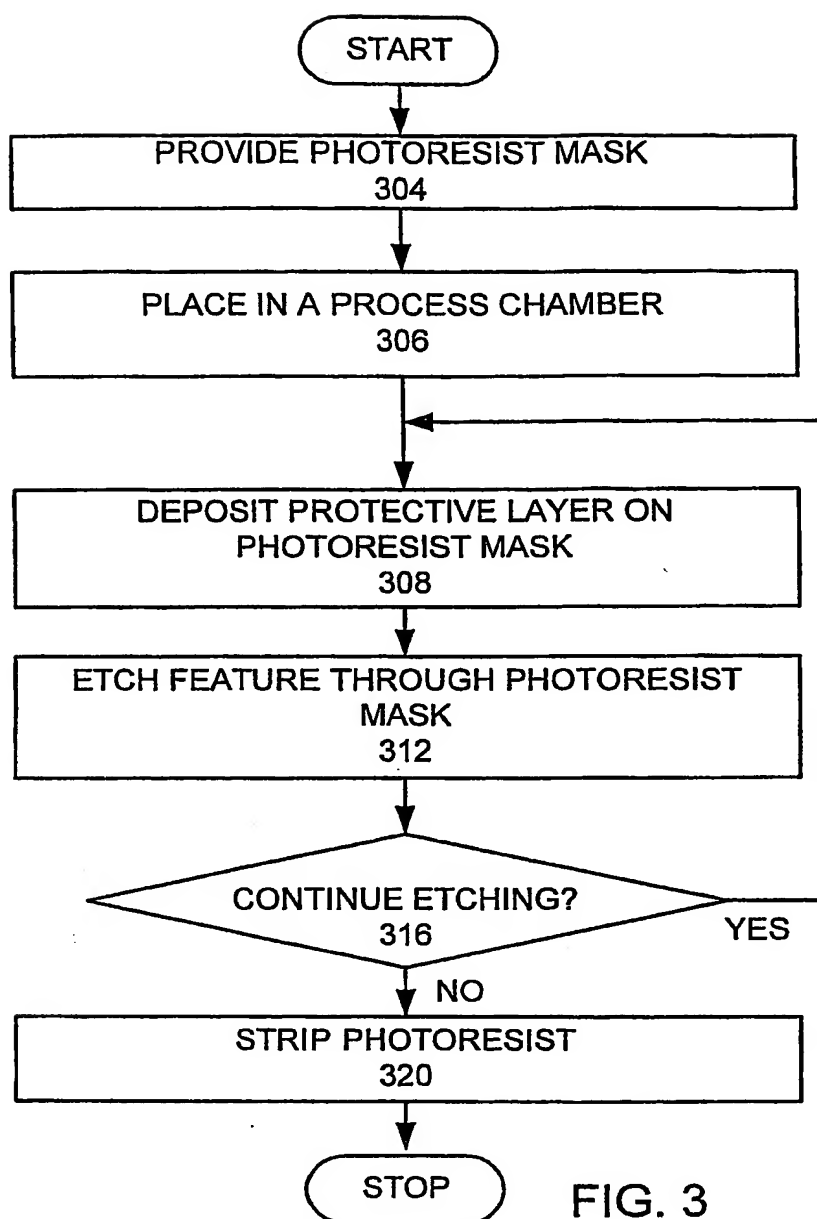


FIG. 3

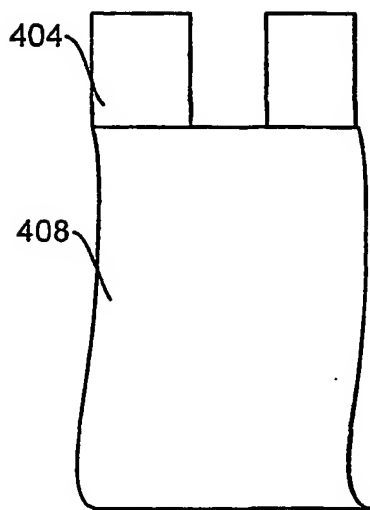


FIG. 4A

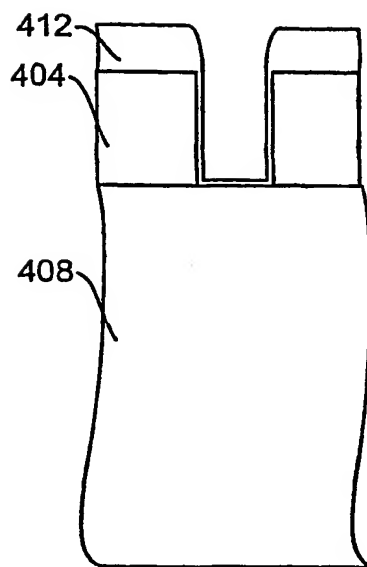


FIG. 4B

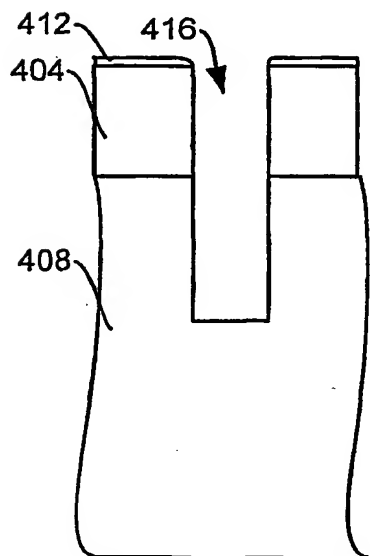


FIG. 4C

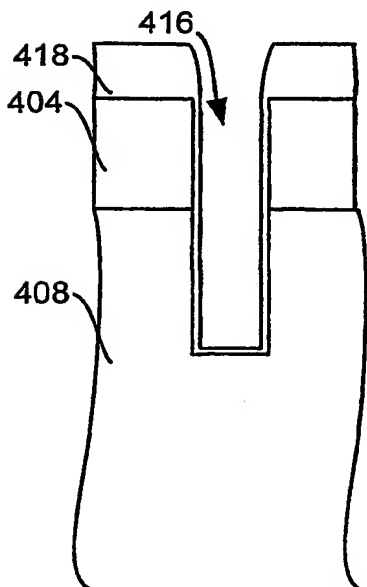


FIG. 4D

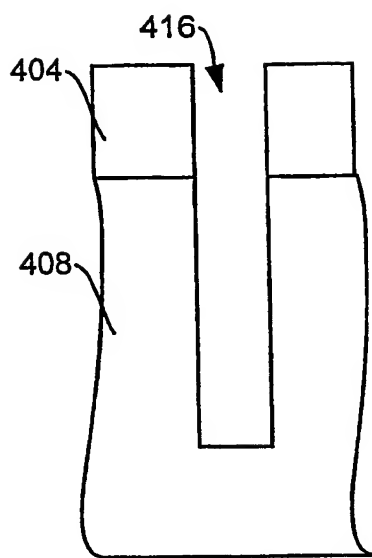


FIG. 4E

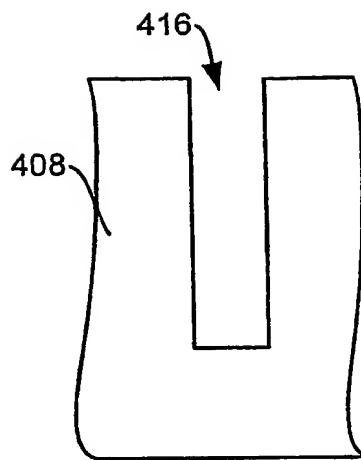


FIG. 4F

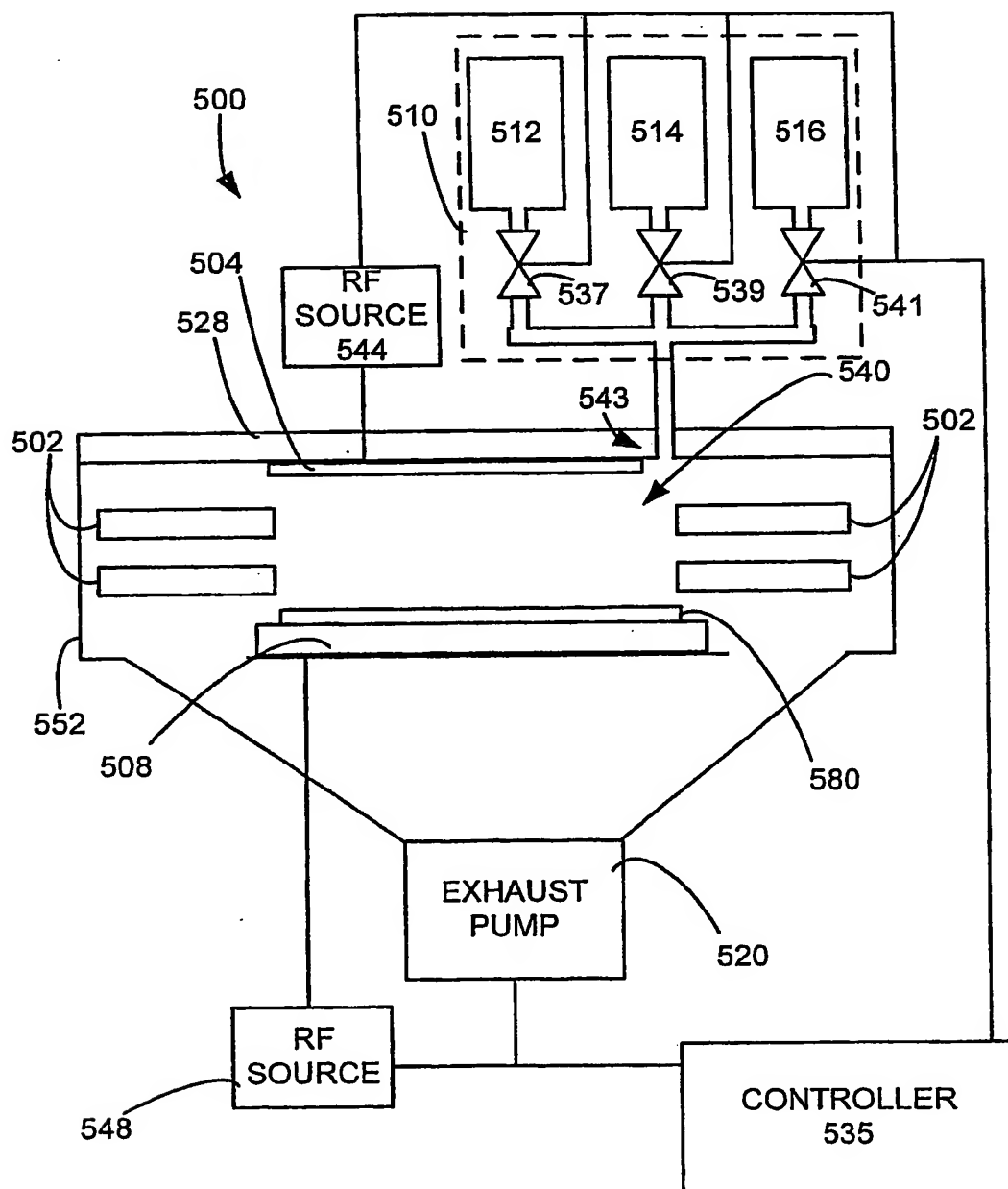


FIG. 5



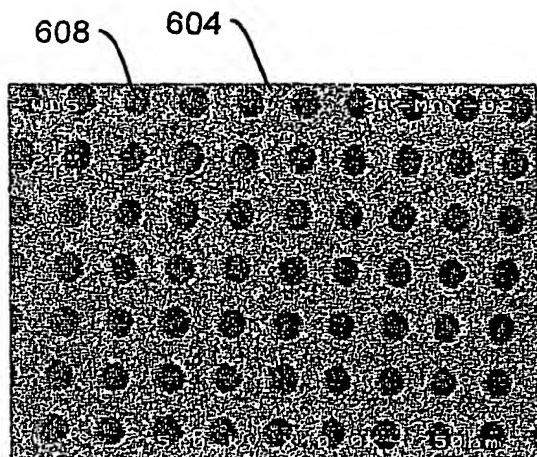


FIG. 6

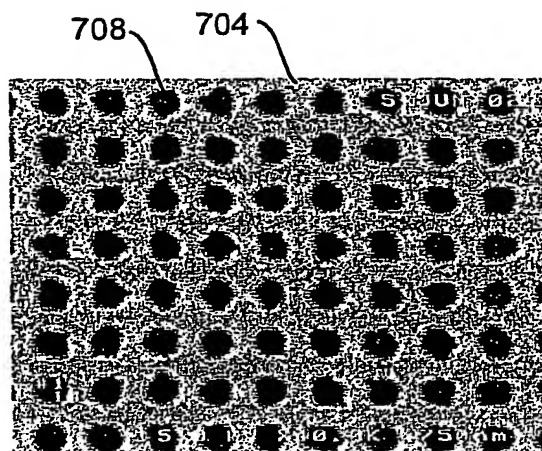
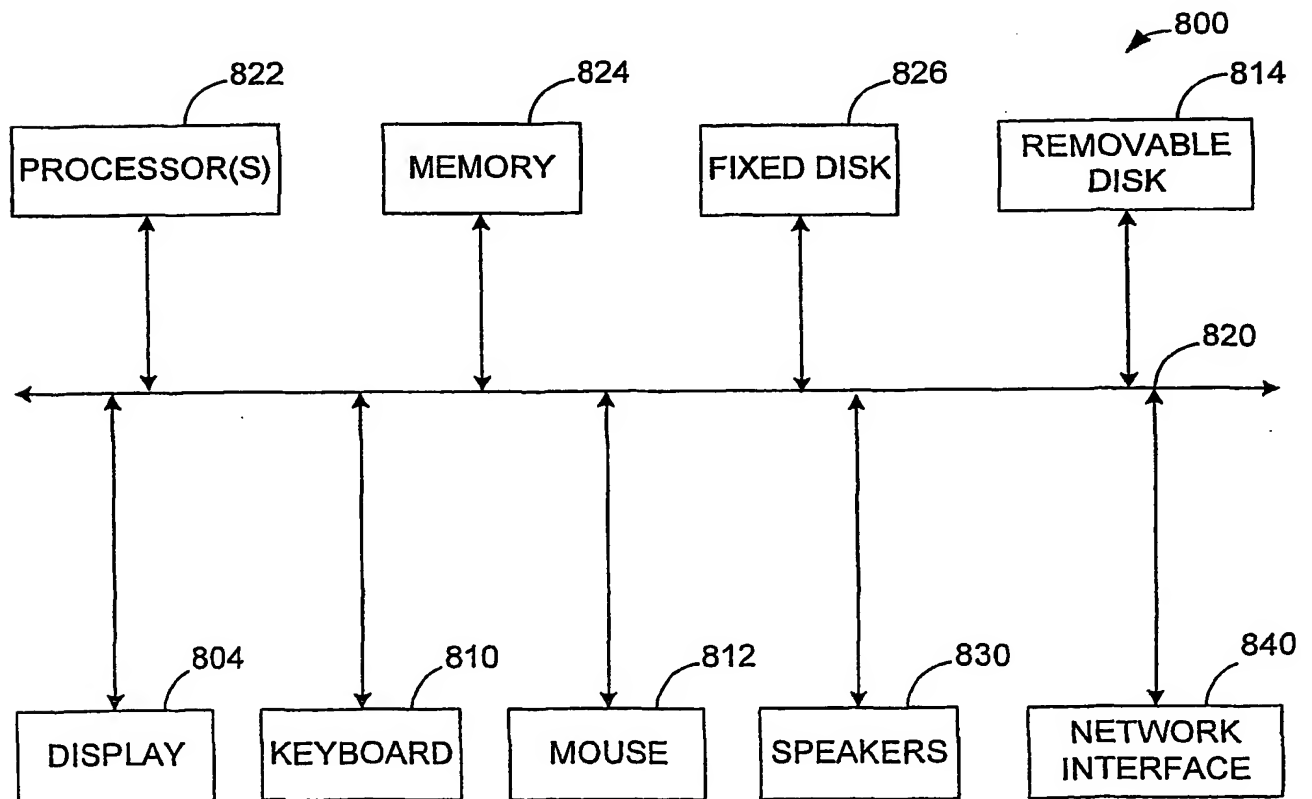
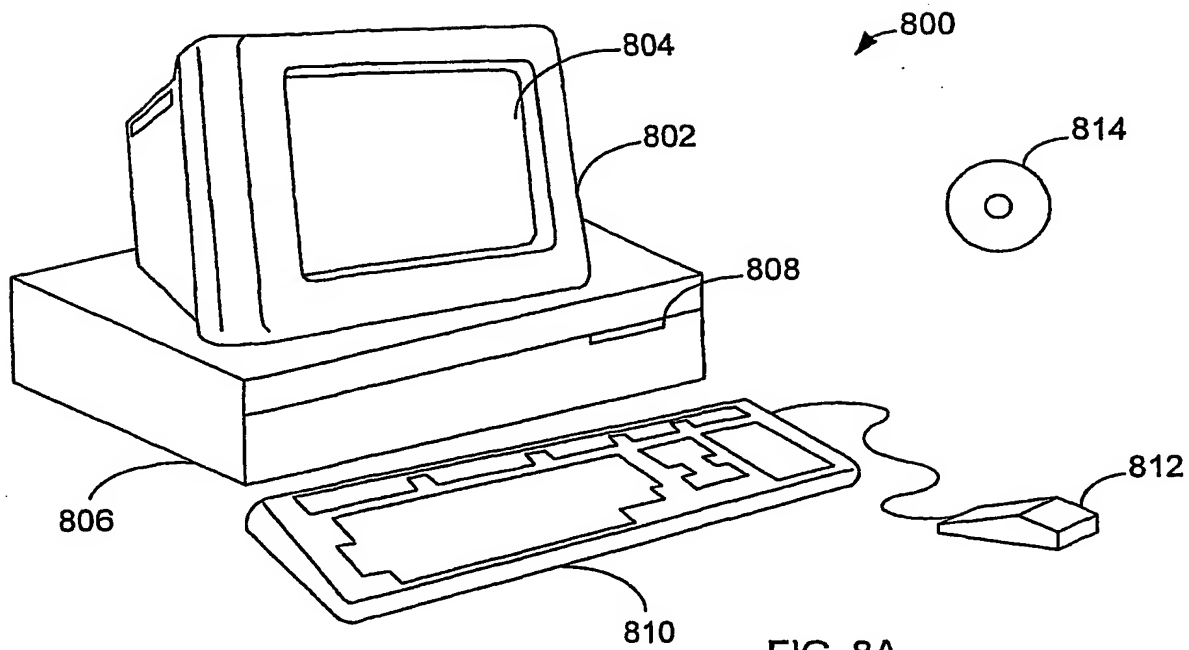
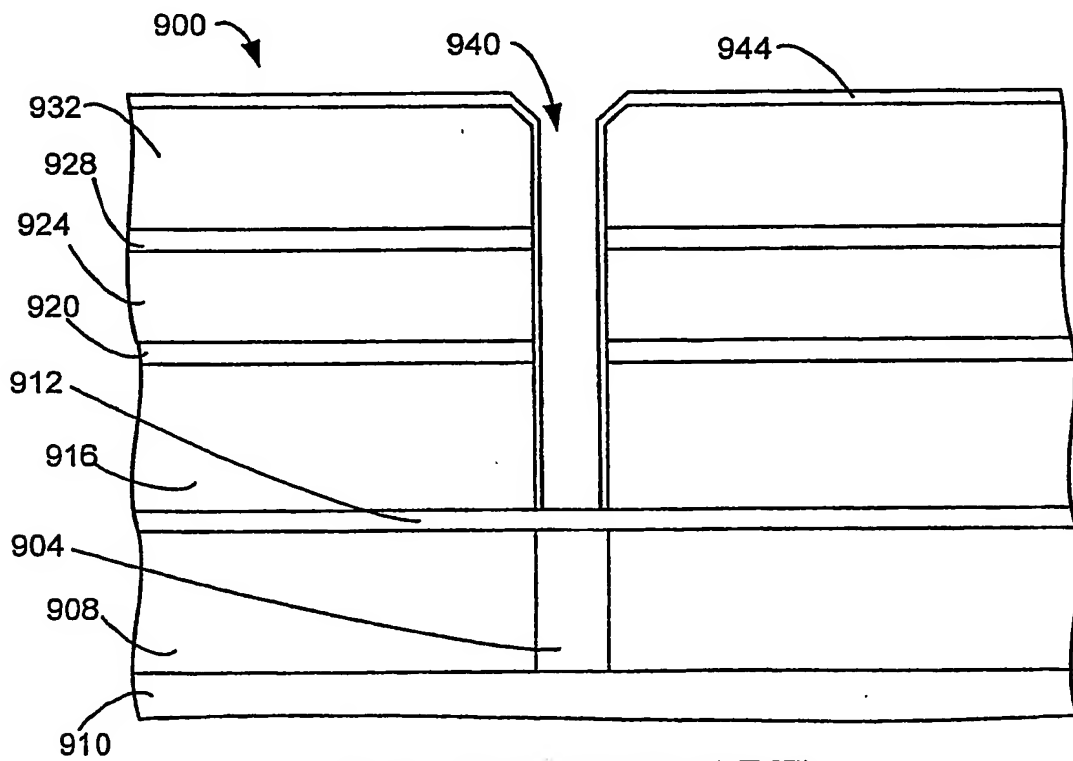
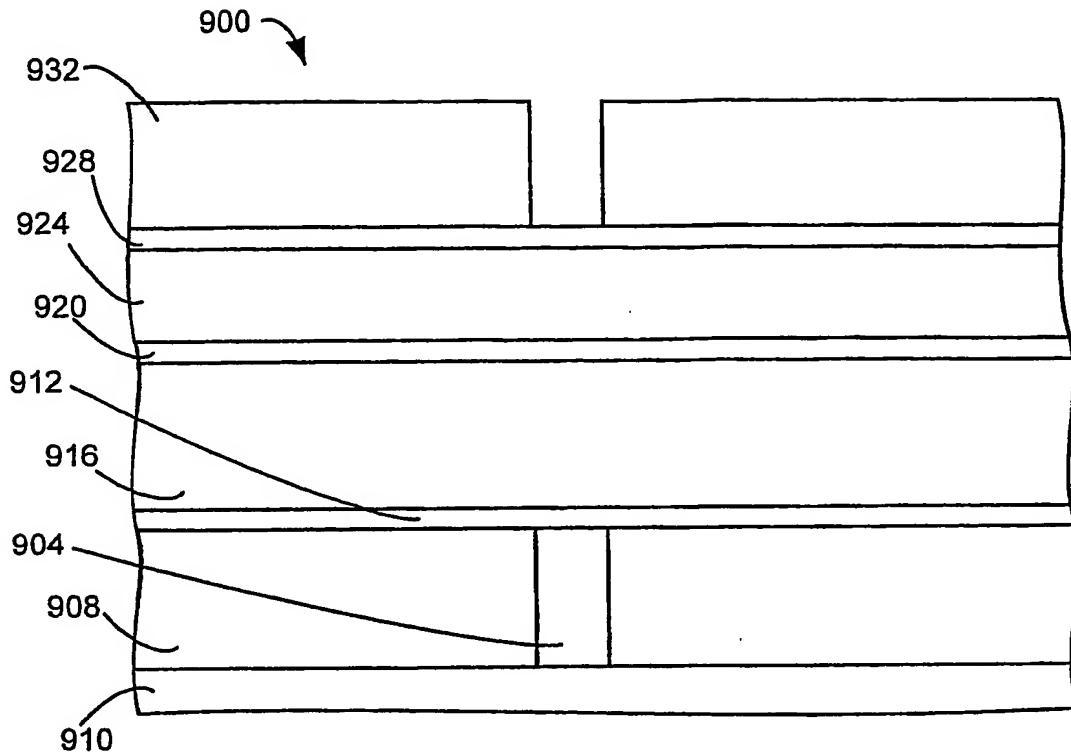
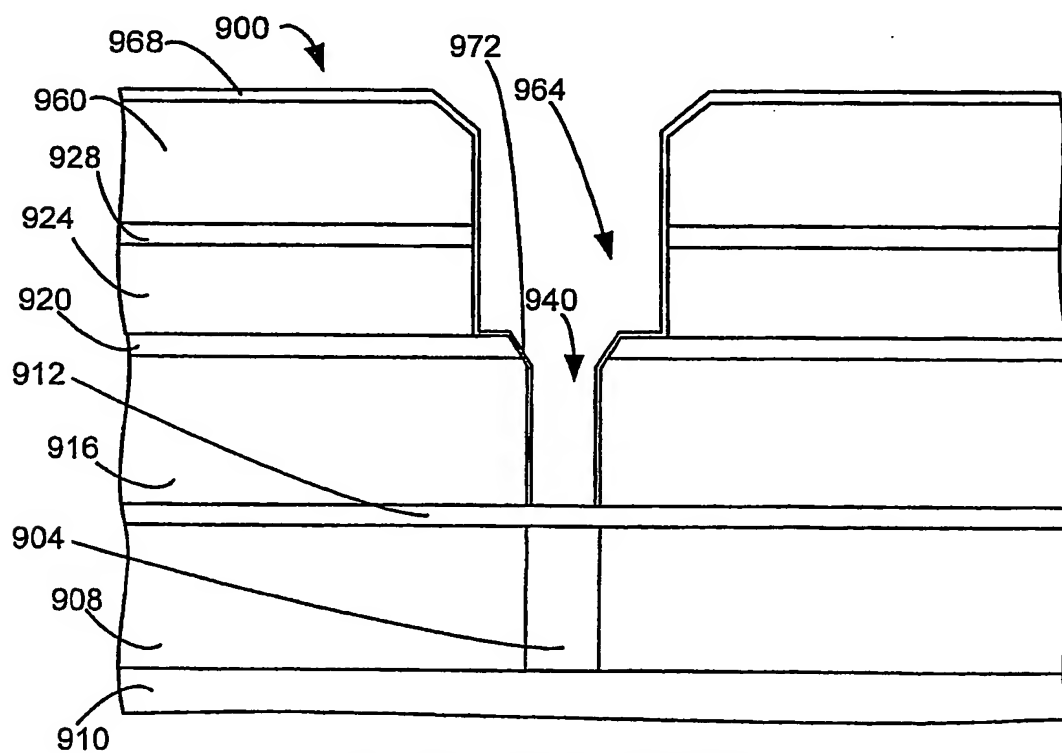
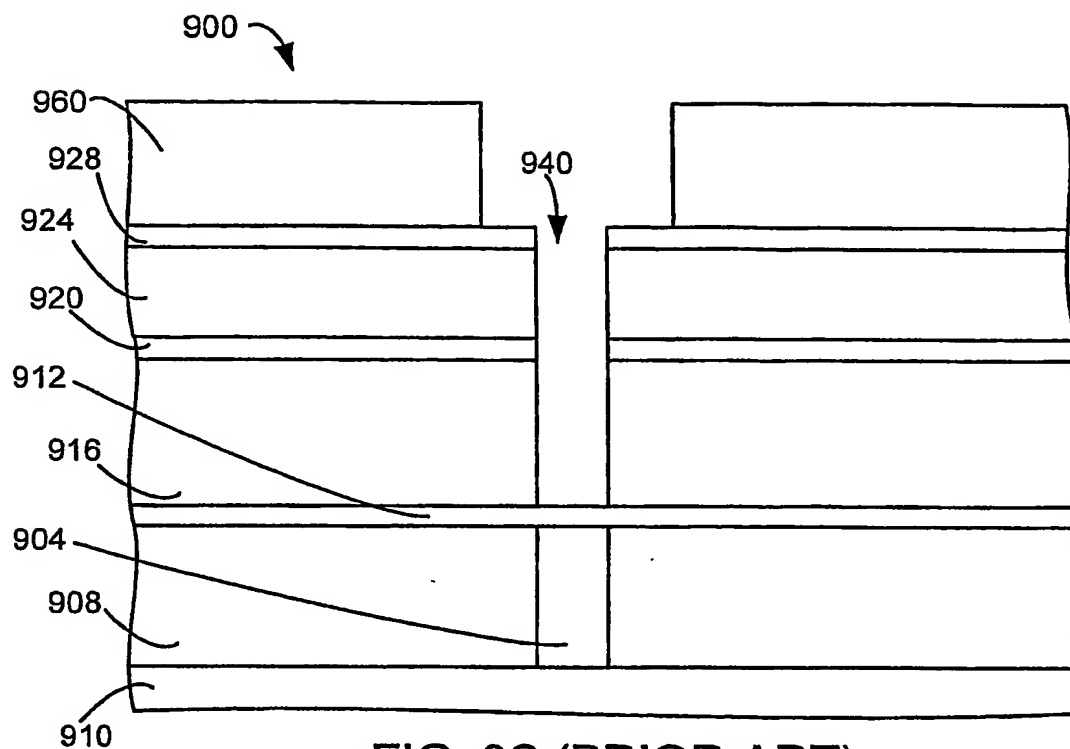


FIG. 7







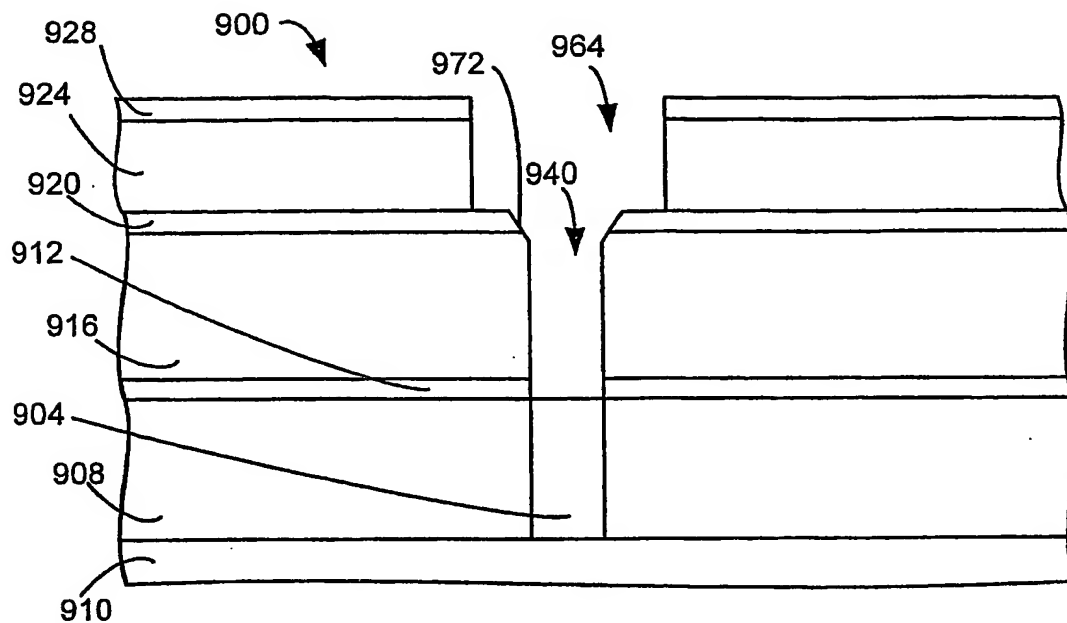


FIG. 9E (PRIOR ART)

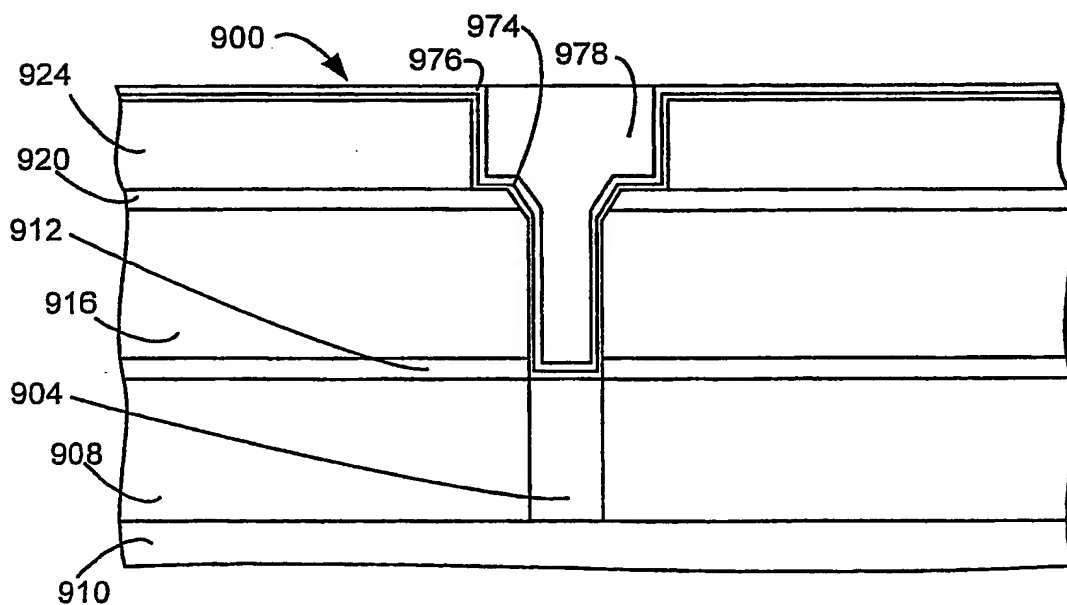


FIG. 9F (PRIOR ART)

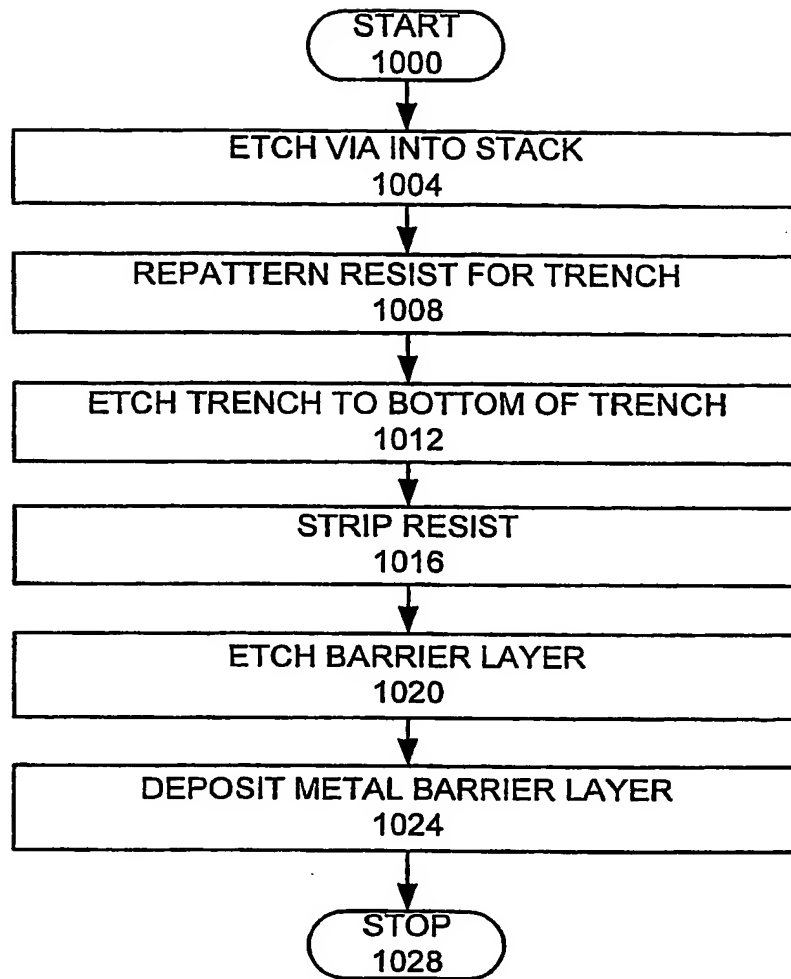
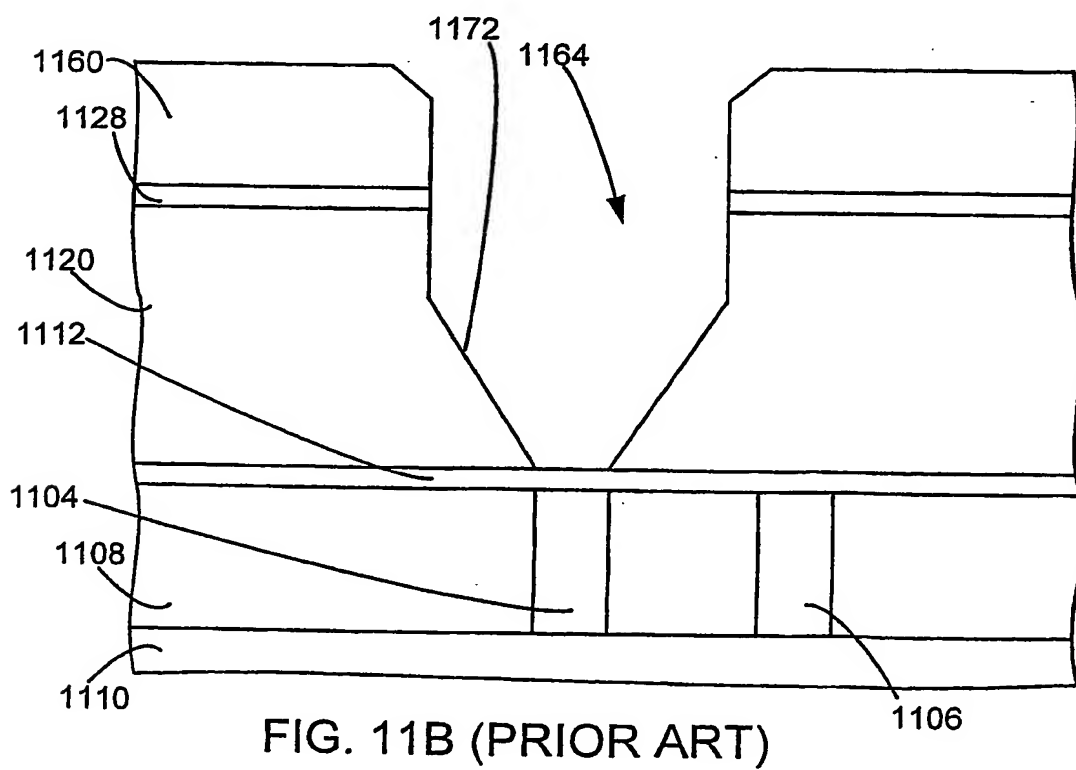
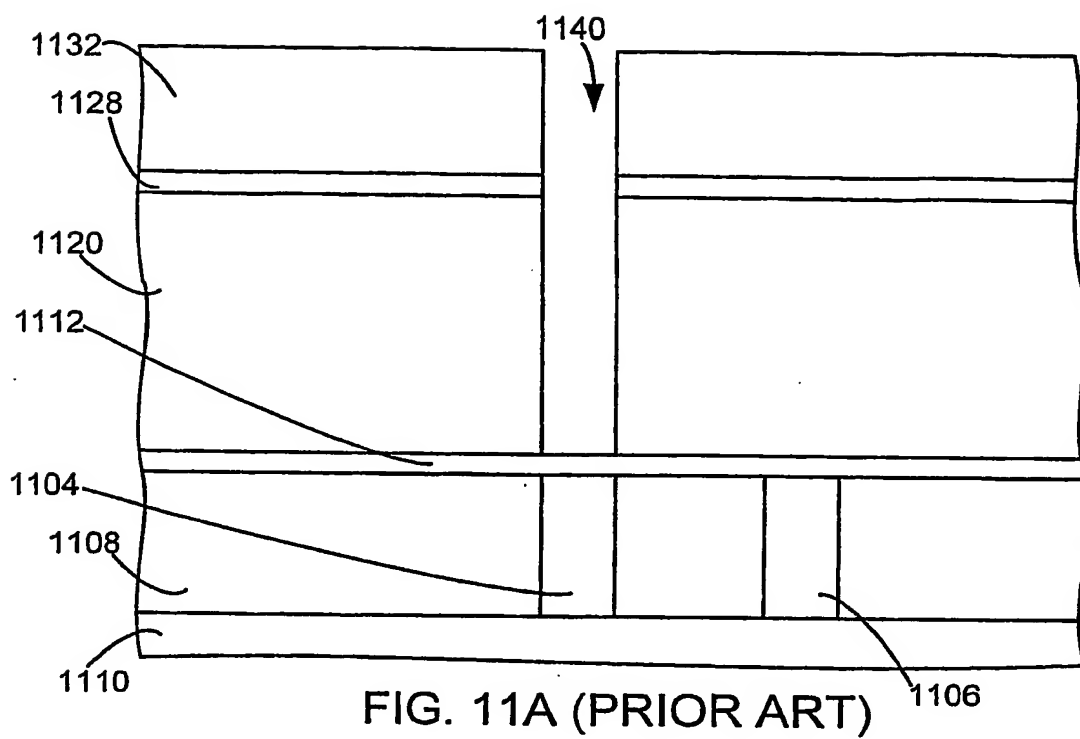


FIG. 10 (PRIOR ART)



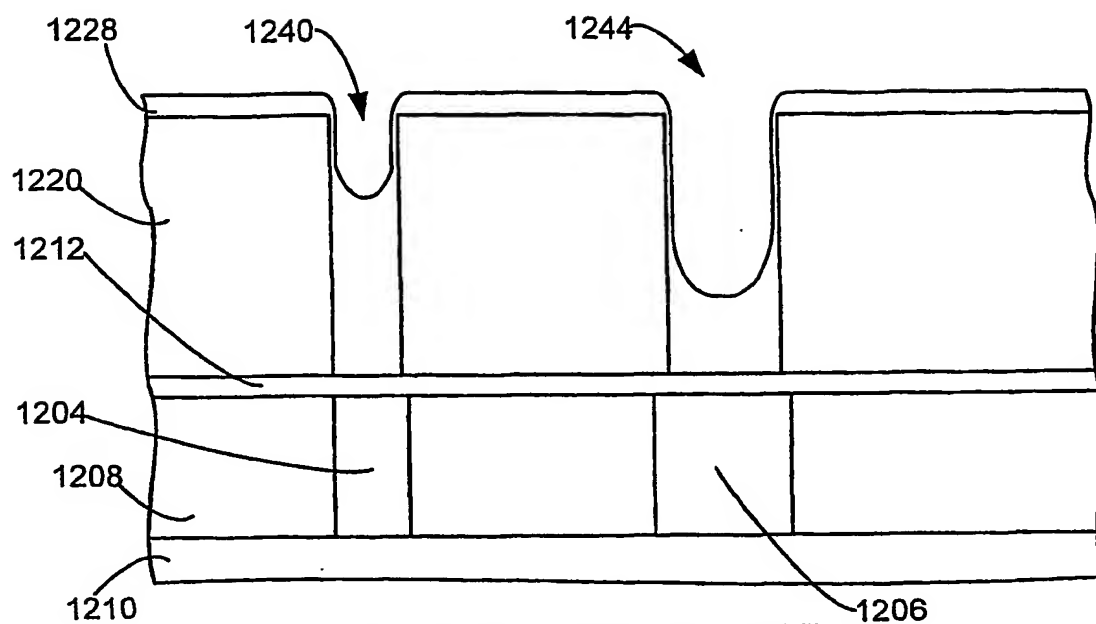


FIG. 12A (PRIOR ART)

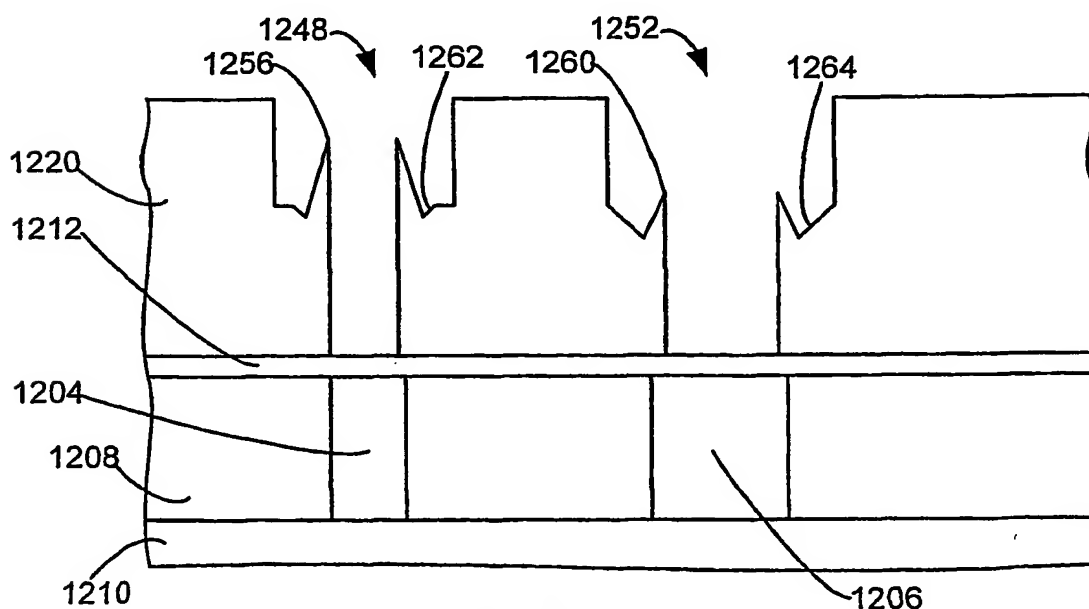


FIG. 12B (PRIOR ART)



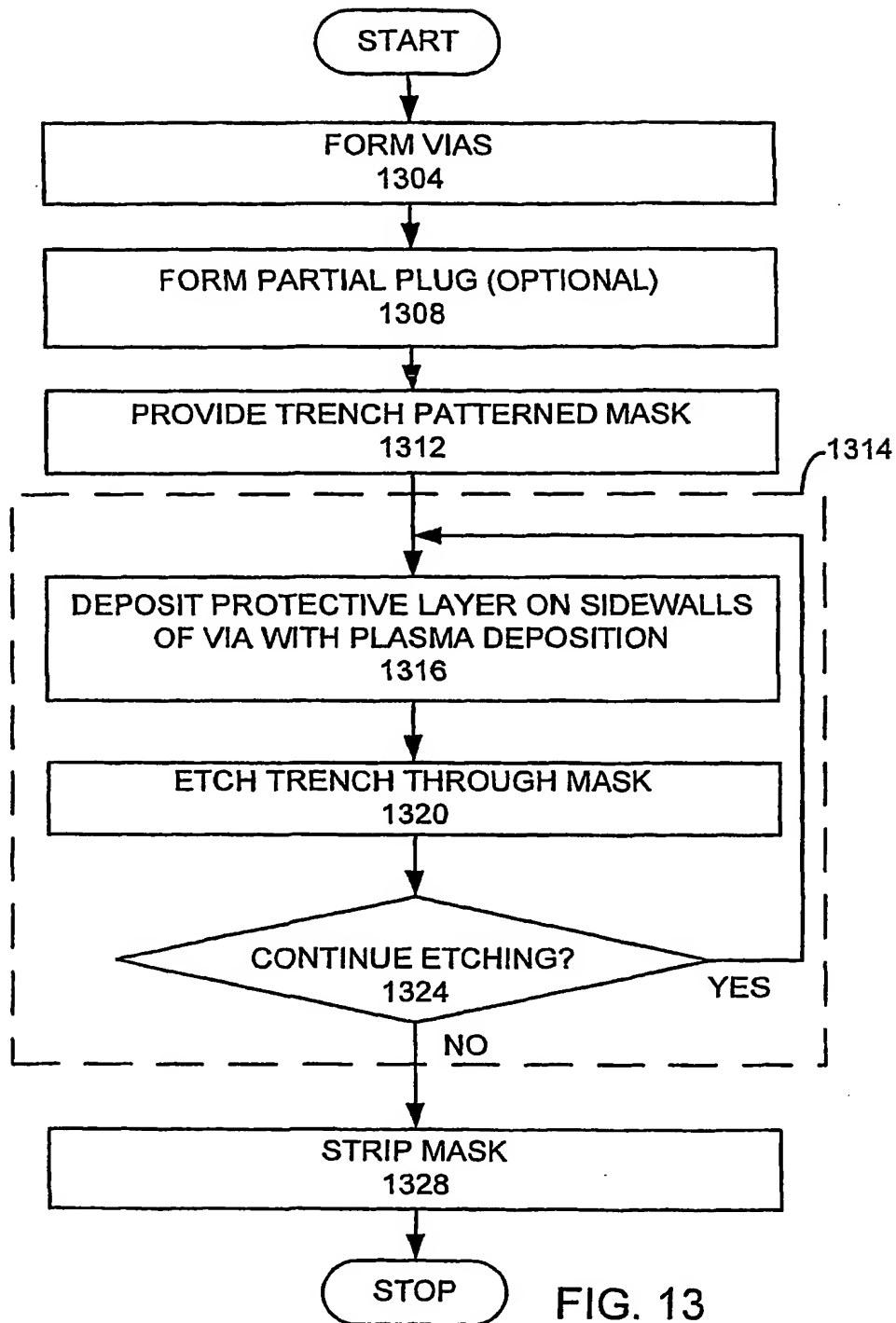
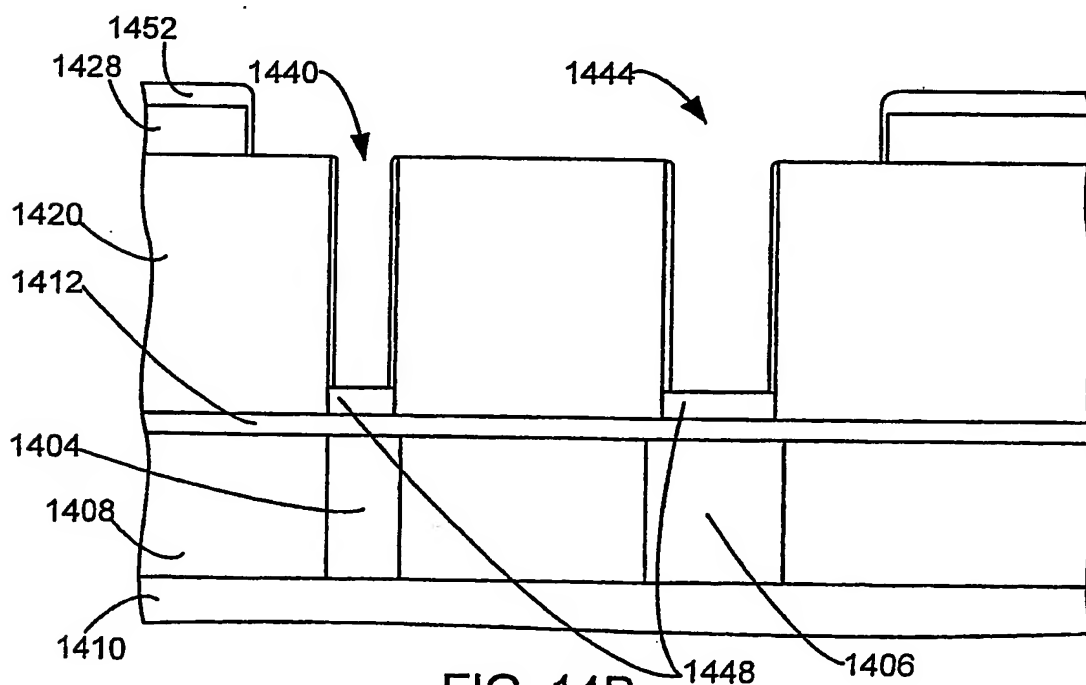
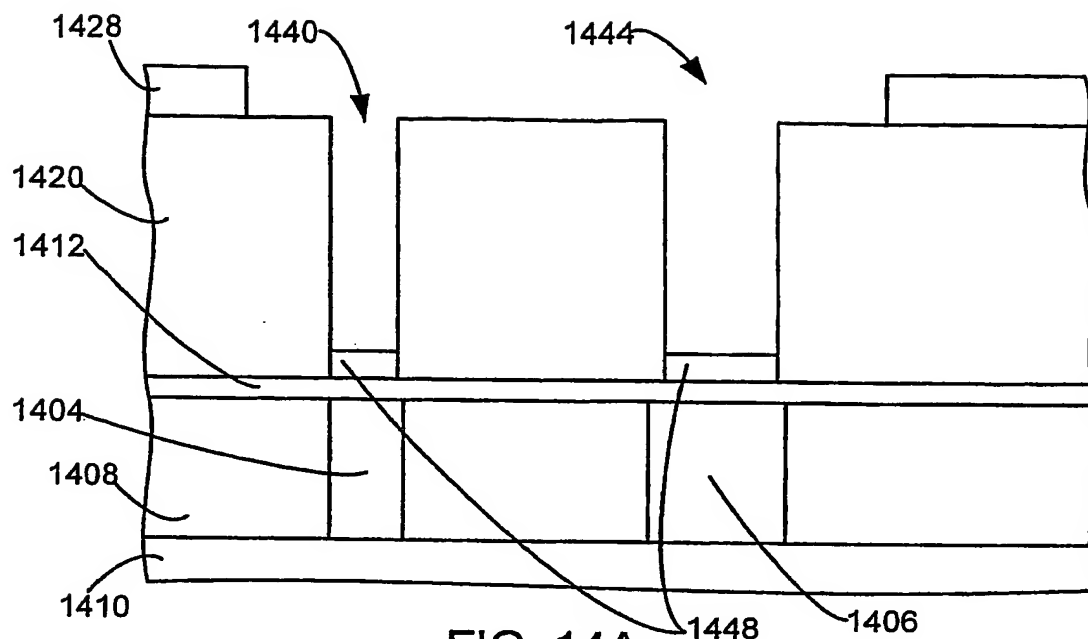
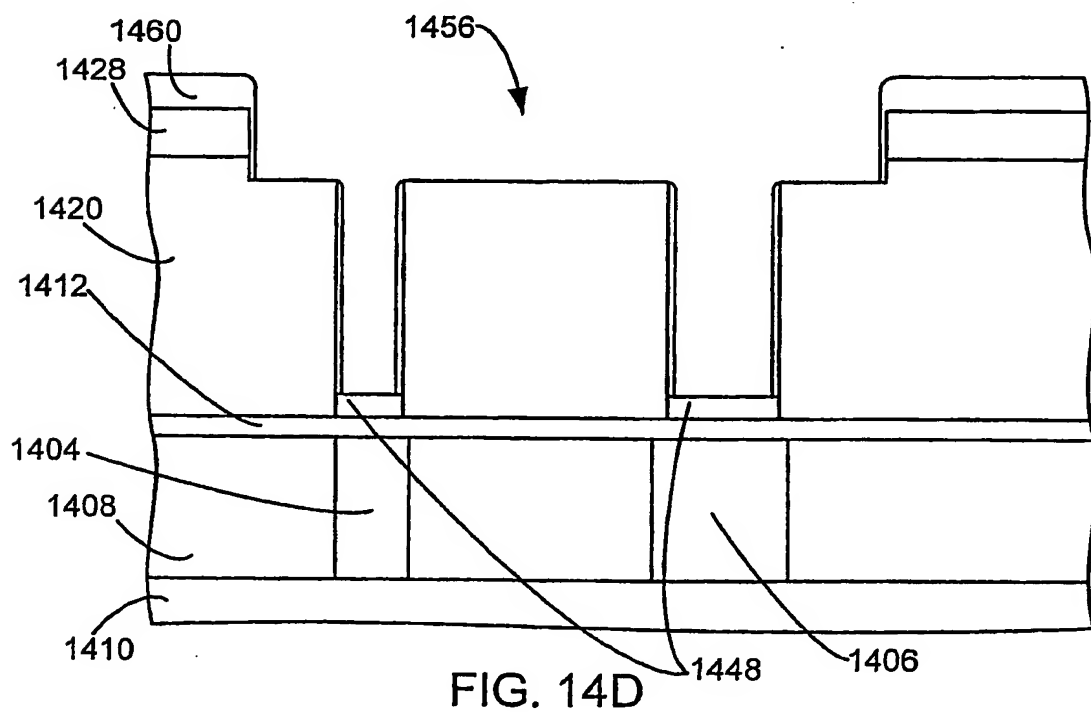
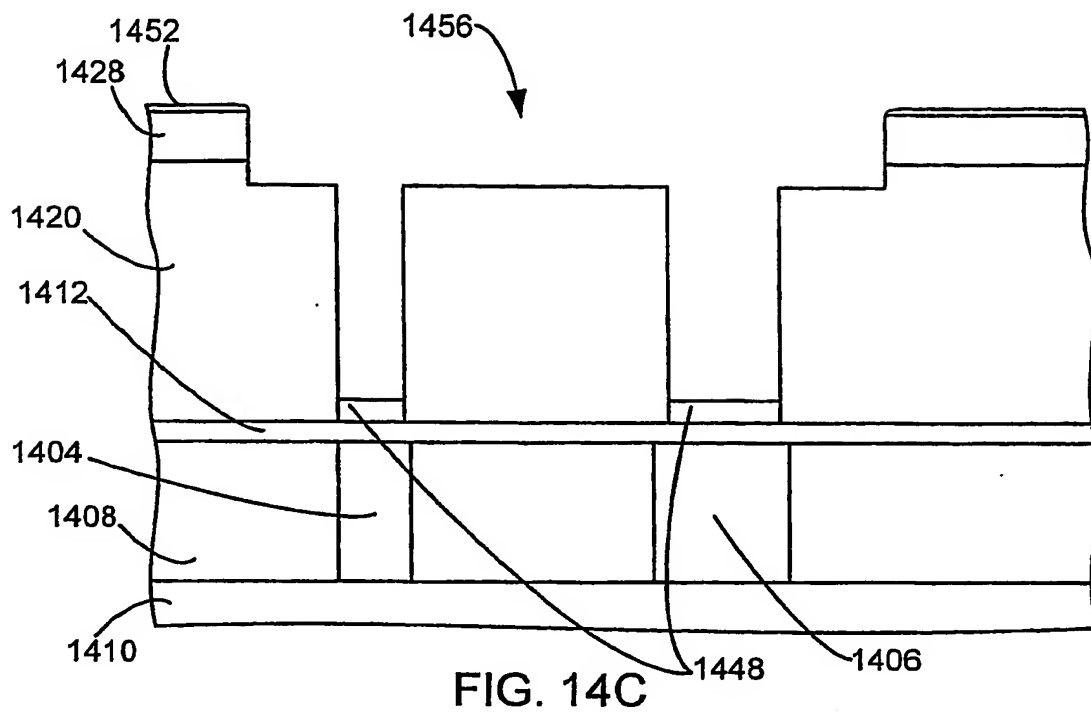


FIG. 13





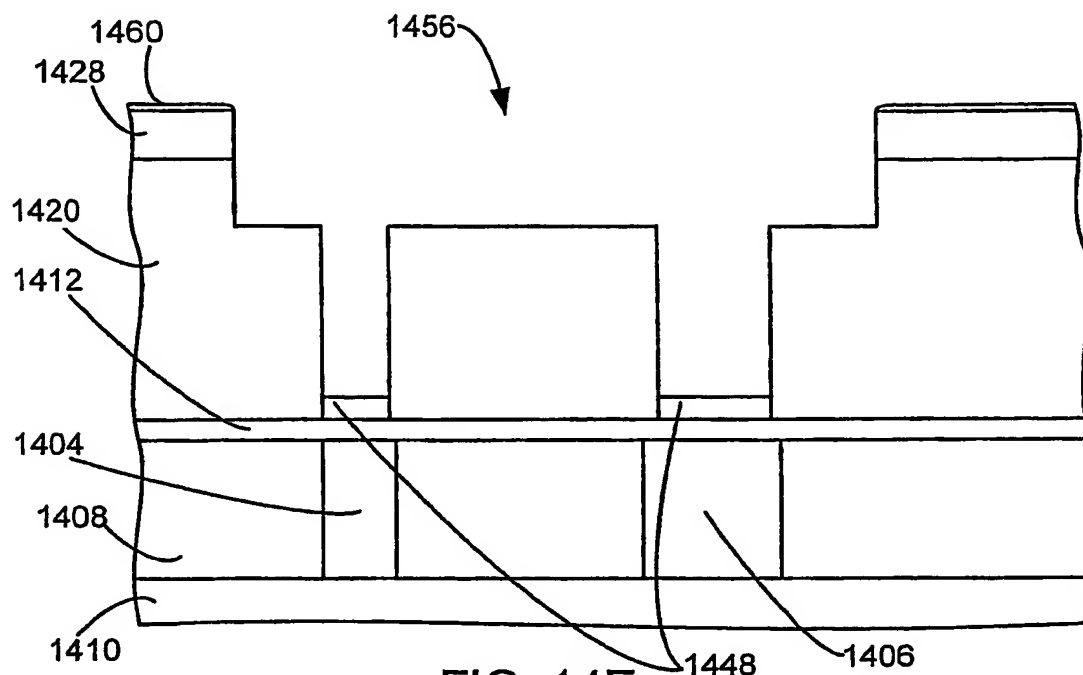


FIG. 14E

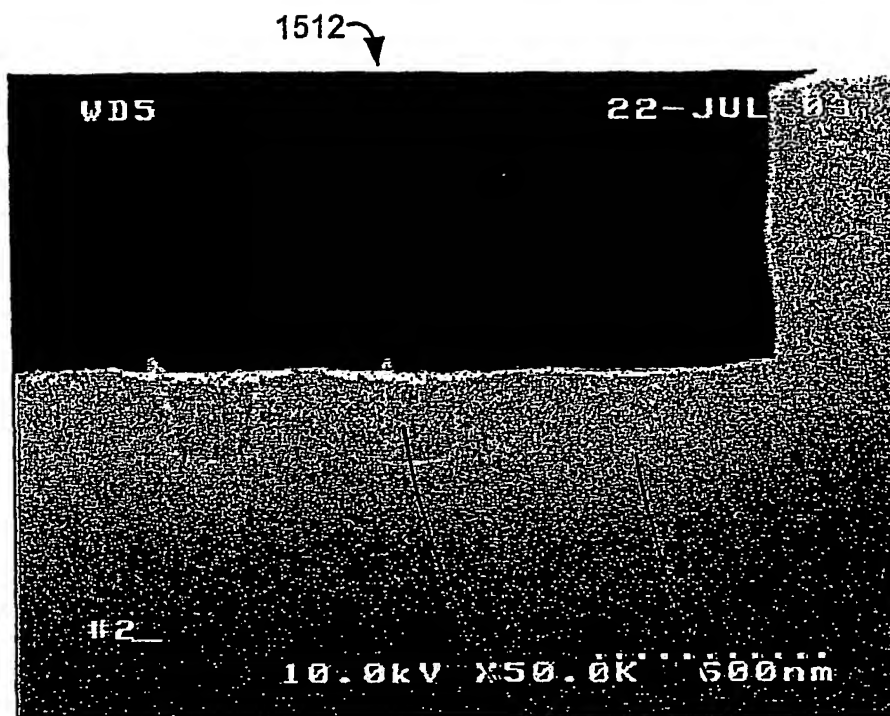


FIG. 15A

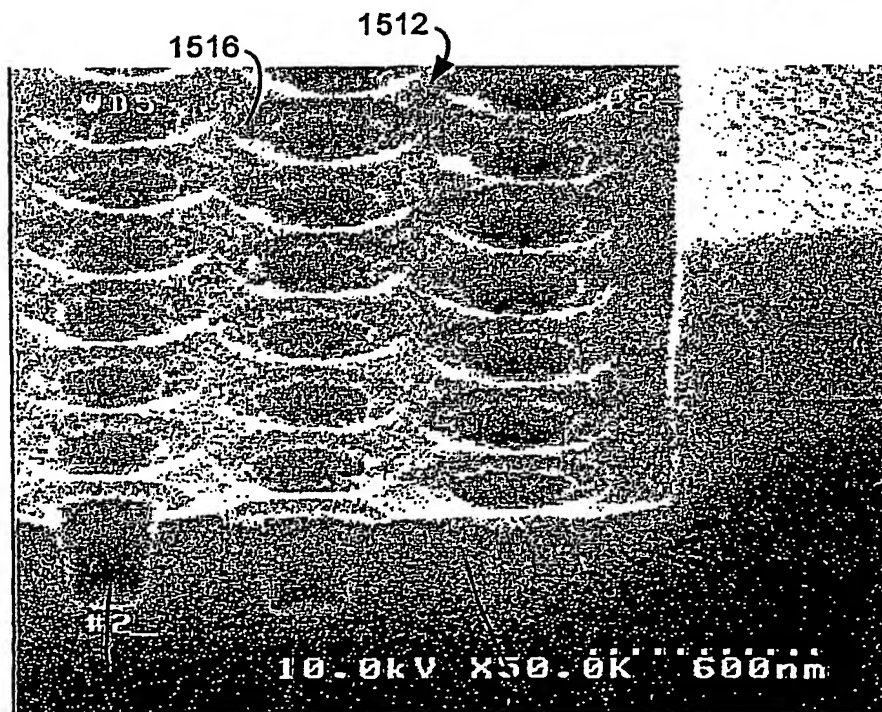


FIG. 15B

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
22 April 2004 (22.04.2004)

PCT

(10) International Publication Number  
**WO 2004/034445 A3**

(51) International Patent Classification<sup>7</sup>: **H01L 21/311**,  
21/768

(21) International Application Number:  
PCT/US2003/031712

(22) International Filing Date: 6 October 2003 (06.10.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/417,806 11 October 2002 (11.10.2002) US  
10/295,601 14 November 2002 (14.11.2002) US  
10/674,675 29 September 2003 (29.09.2003) US

(71) Applicants (for all designated States except US): LAM  
RESEARCH CORPORATION [US/US]; 4650 Cushing

Parkway, Fremont, CA 94538 (US). **LI, Lumin** [US/US];  
3480 Tracy Drive, Santa Clara, CA 95051 (US). **SAD-  
JADI, Reza** [US/US]; 19413 Vineyard Lane, Saratoga, CA  
95070 (US).

(72) Inventor; and

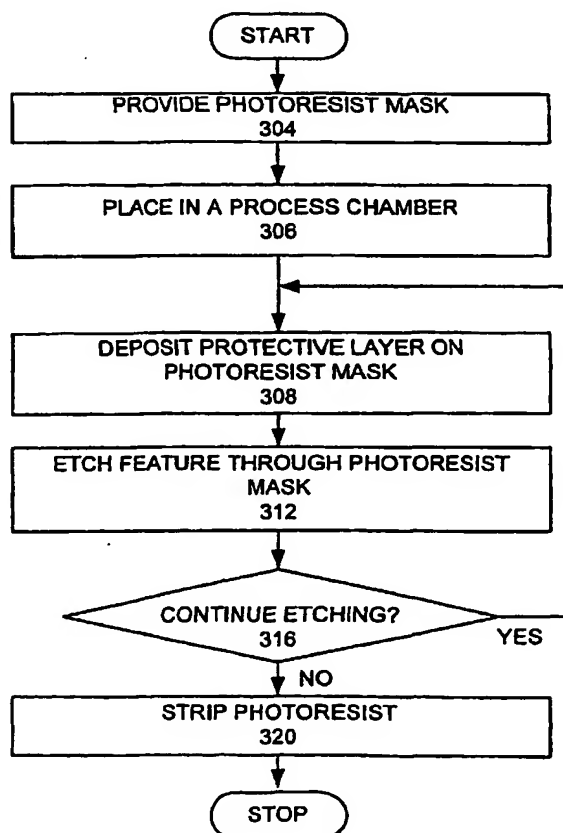
(75) Inventor/Applicant (for US only): **HUANG, Zhisong**  
[US/US]; 5972 Roxie Terrace, Fremont, CA 94555 (US).

(74) Agent: **OLYNICK, Mary, R.**; Beyer Weaver & Thomas,  
LLP, P.O. Box 778, Berkeley, CA 94704-0778 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,  
SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,  
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

[Continued on next page]

(54) Title: A METHOD FOR PLASMA ETCHING PERFORMANCE ENHANCEMENT



(57) Abstract: A method for etching a feature in a layer through an etching mask is provided. A protective layer is formed on exposed surfaces of the etching mask and vertical sidewalls of the feature with a passivation gas mixture. The feature is etched through the etching mask with reactive etching mixtures containing at least one etching chemical and at least one passivation chemical.

WO 2004/034445 A3



(84) **Designated States (regional):** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

(88) **Date of publication of the international search report:**  
12 August 2004

**Published:**

— *with international search report*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

# INTERNATIONAL SEARCH REPORT

Inter. al Application No  
PCT/US 03/31712

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 H01L21/311 H01L21/768

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	US 6 569 774 B1 (TRAPP SHANE J) 27 May 2003 (2003-05-27) the whole document	1,2,9-19
X	----- PATENT ABSTRACTS OF JAPAN vol. 2000, no. 20, 10 July 2001 (2001-07-10) -& JP 2001 068462 A (SAMSUNG ELECTRONICS CO LTD), 16 March 2001 (2001-03-16) abstract paragraph [0001] - paragraph [0007] paragraphs [0071], [0088] - [0092]	1-22, 39-41
X	----- US 6 326 307 B1 (KOMATSU TAKEHITO ET AL) 4 December 2001 (2001-12-04)  column 8, line 21 - column 9; figure 12 ----- -/--	1-7, 9-12, 16-19

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

17 February 2004

Date of mailing of the international search report

29. 06. 2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Szarowski, A



## INTERNATIONAL SEARCH REPORT

Inte      ial Application No

PCT/US 03/31712

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 100 59 836 A (INFINEON TECHNOLOGIES AG) 13 June 2002 (2002-06-13)  column 7 - column 8 -----	1,2, 9-12,16, 18,19
X	EP 0 822 582 A (SURFACE TECH SYS LTD) 4 February 1998 (1998-02-04)  page 4, line 20 - line 40 page 6, line 23 - line 34 -----	1,2, 9-12,16, 18-22, 39-41
X	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 11, 26 December 1995 (1995-12-26) -& JP 07 226397 A (TOKYO ELECTRON LTD), 22 August 1995 (1995-08-22) abstract -----	1,2, 9-12,16, 18-22, 39-41
X	US 6 025 255 A (LEE DANIEL HAO-TIEN ET AL) 15 February 2000 (2000-02-15) column 5 - column 6 -----	1,2,9-19
X	US 6 074 959 A (DING JIAN ET AL) 13 June 2000 (2000-06-13)  figure 2; examples 9,10 -----	1,2, 9-12,14, 16-22, 39-41
X	WO 00/30168 A (APPLIED MATERIALS INC ;HUNG HOIMAN RAYMOND (US); SHAN HONGCHING (U) 25 May 2000 (2000-05-25) the whole document -----	1,2, 9-22, 39-41
X	US 6 403 491 B1 (KIM YUNSANG ET AL) 11 June 2002 (2002-06-11)  the whole document -----	1-4, 9-12, 16-22, 39-41
X	US 4 795 529 A (KAWAHARA HIRONOBU ET AL) 3 January 1989 (1989-01-03)  the whole document -----	1,2, 9-13, 18-22, 39-41
X	US 5 562 801 A (NULTY JAMES E) 8 October 1996 (1996-10-08)  column 13 - column 14; figures 18-20 -----	1,2, 9-12,16, 18,19
A	US 5 942 446 A (YU CHEN-HUA ET AL) 24 August 1999 (1999-08-24) the whole document -----	1-19
	----- -/--	

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 03/31712

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 5 882 535 A (DONOHOE KEVIN G ET AL)  16 March 1999 (1999-03-16)  the whole document  -----</p>	1-19

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 03/31712

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-22, 39-41

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-22,39-41

A method for etching a feature in a layer through an etching mask comprising:  
forming a protective coating on exposed surfaces of the etching mask and vertical sidewalls of the feature with a passivation gas mixture; and  
etching the feature through the etching mask with reactive etching mixtures containing at least one etching chemical and at least one passivation chemical.  
Apparatus therefor.

---

2. claims: 23-38

A method for forming a dual damascene feature comprising:  
forming vias in an etch layer;  
providing a trench patterned mask over the etch layer;  
etching a trench, wherein etching the trench comprises a cycle of:  
forming protective sidewalls over the sidewalls of the vias;  
and  
etching a trench through the trench patterned mask; and  
stripping the mask.  
Semiconductor formed by the method.  
Apparatus therefor.

---

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/31712

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6569774	B1	27-05-2003	US 2003162395 A1	28-08-2003
JP 2001068462	A	16-03-2001	KR 2001015338 A	26-02-2001
			US 6617253 B1	09-09-2003
US 6326307	B1	04-12-2001	NONE	
DE 10059836	A	13-06-2002	DE 10059836 A1	13-06-2002
EP 0822582	A	04-02-1998	AT 251341 T	15-10-2003
			DE 69725245 D1	06-11-2003
			EP 1357584 A2	29-10-2003
			EP 0822582 A2	04-02-1998
			JP 10135192 A	22-05-1998
			JP 2004119994 A	15-04-2004
			US 6051503 A	18-04-2000
JP 07226397	A	22-08-1995	US 5728253 A	17-03-1998
US 6025255	A	15-02-2000	NONE	
US 6074959	A	13-06-2000	JP 2001517868 T	09-10-2001
			TW 442866 B	23-06-2001
			US 6183655 B1	06-02-2001
			WO 9916110 A2	01-04-1999
			US 6361705 B1	26-03-2002
WO 0030168	A	25-05-2000	US 6174451 B1	16-01-2001
			US 6387287 B1	14-05-2002
			JP 2002530863 T	17-09-2002
			WO 0030168 A1	25-05-2000
			US 6602434 B1	05-08-2003
			US 6613691 B1	02-09-2003
			US 2003000913 A1	02-01-2003
US 6403491	B1	11-06-2002	EP 1334514 A2	13-08-2003
			JP 2004513516 T	30-04-2004
			WO 0237541 A2	10-05-2002
US 4795529	A	03-01-1989	JP 2107218 C	06-11-1996
			JP 8008237 B	29-01-1996
			JP 63288021 A	25-11-1988
			KR 9007687 B1	18-10-1990
US 5562801	A	08-10-1996	US 5468342 A	21-11-1995
			EP 0721205 A2	10-07-1996
			JP 9027483 A	28-01-1997
US 5942446	A	24-08-1999	NONE	
US 5882535	A	16-03-1999	NONE	

**AMENDED CLAIMS**

received by the International Bureau on 09 August 2004  
claim 1-41 are replaced by new claims 1-55.

1. A method for etching a feature in a layer through an etching mask comprising:  
forming a protective coating on exposed surfaces of the etching mask and  
5 vertical sidewalls of the feature with a passivation gas mixture; and  
etching the feature through the etching mask with reactive etching mixtures  
containing at least one etching chemical and at least one passivation chemical.
2. The method, as recited in claim 1, wherein the etching comprises providing an  
10 ion bombardment energy of greater than 200 electron volts to the substrate.
3. The method, as recited in any of claims 1 to 2, wherein the etching chemical  
contains a polymer former and an etch enabler.
- 15 4. The method, as recited in any of claims 1 to 3, wherein the forming the  
protective coating and etching are performed in a common plasma processing  
chamber.
5. The method, as recited in any of claims 1 to 4, wherein the forming the  
20 protective coating uses a non-directional deposition and the etching step uses a  
directional etching.
6. The method, as recited in any of claims 1 to 5, wherein the forming the  
protective coating is a non-etching or a negligibly etching deposition.  
25
7. The method, as recited in any of claims 1 to 6, wherein the forming the  
protective coating is selected from at least one of chemical vapor deposition and  
sputtering.
- 30 8. The method, as recited in any of claims 1 to 7, wherein the layer is only a  
single layer, wherein the feature is etched only in the single layer during the forming  
the protective coating and etching the feature, wherein the forming the protective  
coating and etching are performed in a sequentially alternating fashion at least four  
times.

9. The method, as recited in any of claims 1 to 8, wherein the etching mask is a photoresist mask 193 nm or below generation.

10 The method, as recited in any of claims 1 to 9, wherein the protective coating  
5 is formed preferentially on the exposed areas of the etching mask and the vertical sidewalls of the features.

11. The method, as recited in any of claims 1 to 10, wherein the passivation gas  
mixture releases a polymerizing agent that is more chemically active to the layer than  
10 the mask materials.

12. The method, as recited in any of claims 10 to 11, wherein directional energetic  
ions are used to preferentially prevent deposition from accumulating at the horizontal  
surfaces of the layer during the step of the formation of protective coating by  
15 activating a removal mechanism of the coating on selectively the surface of the layer.

13 The method, as recited in any of claims 1 to 12, wherein passivation gas  
mixture is a hydrofluorocarbon with F:C ratio of less than 2:1.

20 14. The method, as recited in any of claims 1 to 13, wherein at least one of the  
passivation chemical is one of the  $\text{CH}_3\text{F}$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{C}_2\text{H}_5\text{F}$ ,  $\text{C}_2\text{H}_4\text{F}_2$ ,  $\text{C}_3\text{H}_7\text{F}$ ,  $\text{C}_3\text{H}_6\text{F}_2$ ,  
 $\text{C}_2\text{H}_3\text{F}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_2\text{H}_2$ .

15. The method, as recited in any of claims 1 to 14, wherein the passivation gas  
25 mixture is a mixture of Ar and  $\text{CH}_3\text{F}$ .

16. The method, as recited in any of claims 1 to 15, wherein the ion energy  
provided in the passivation step is greater than 100 electron volts.

30 17. The method, as recited in any of claims 1 to 16, wherein at least one of the  
etching chemicals is  $\text{C}_4\text{F}_6$ .

18. The method as recited in any of claims 1 to 17, wherein at least one of the RF  
frequencies used for the discharge is one of the 2MHz, 27MHz and 60MHz.

35

19. The method, as recited in any of claims 1 to 18, wherein the RF discharge frequencies consist of a combination a lower frequency in the range of 400KHz to 13.56MHz and another higher frequency in the range of 27MH to 120MHz.
- 5 20. An apparatus for etching a layer under an etch mask, wherein the layer is supported by a substrate, comprising:
- a plasma processing chamber, comprising:
    - a chamber wall forming a plasma processing chamber enclosure;
    - a substrate support for supporting a substrate within the plasma
  - 10 processing chamber enclosure;
  - a pressure regulator for regulating the pressure in the plasma processing chamber enclosure;
  - at least one electrode for providing power to the plasma processing chamber enclosure for sustaining a plasma;
  - 15 a gas inlet for providing gas into the plasma processing chamber enclosure; and
  - a gas outlet for exhausting gas from the plasma processing chamber enclosure;
  - a deposition gas source;
  - 20 an etchant gas source;
  - a first control valve in fluid connection between the gas inlet of the plasma processing chamber and the deposition gas source;
  - a second control valve in fluid connection between the gas inlet of the plasma processing chamber and the etchant gas source;
  - 25 a controller controllably connected to the first control valve, the second control valve, and the at least one electrode, comprising:
    - at least one processor; and
    - computer readable media, comprising:
      - computer readable code for opening the first control valve for at
      - 30 least one deposition step to provide a deposition gas from the deposition gas source to the plasma processing chamber enclosure;
      - computer readable code for closing the second control valve for the at least one deposition step to prevent etching gas from the etchant gas source from entering the plasma processing chamber enclosure;
      - 35 computer readable code for opening the second control valve



for at least one etching step to provide an etching gas from the etchant gas source to the plasma processing chamber; and

computer readable code energizing the at least one electrode to provide a bias of greater than 250 volts on the substrate for the at least one etching step.

21. The apparatus, as recited in claim 20, further comprising:

a passivation gas source; and

a third control valve in fluid connection between the gas inlet of the plasma processing chamber and the passivation gas source,

wherein the computer readable media further comprises computer readable code for opening a third control valve for the at least one etching step to provide passivation gas from the passivation gas source to the plasma processing chamber.

22. The apparatus, as recited in any of claims 20 to 21, wherein the computer readable media further comprises computer readable code for performing the at least one deposition step and at least one etching step in an alternating fashion for a plurality of times.

23. A method for forming a dual damascene feature, comprising:

forming vias in an etch layer;

providing a trench patterned mask over the etch layer;

etching a trench, wherein the etching the trench comprises a cycle of:

forming protective sidewalls over the sidewalls of the vias; and

etching a trench through the trench patterned mask; and

stripping the mask.

24. The method as recited in claim 23, wherein the trench cycle is repeated at least three times.

25. The method as recited in claim 23, wherein the trench etch cycle is repeated at least five times.

26. The method, as recited in any of claims 23 to 25, wherein the forming the protective sidewalls and etching are performed in a common plasma processing

chamber.

27. The method, as recited in any of claims 23 to 26, wherein the forming the protective sidewalls uses a non-directional deposition and the etching step uses a directional etching.

28. The method, as recited in any of claims 23 to 27, wherein the wafer is bombarded by energetic ions with ionic energy greater than 100 ev during the forming the protective sidewalls.

29. The method, as recited in any of claims 23 to 28, wherein the forming the protective sidewalls is a non-etching or a negligibly etching deposition.

30. The method, as recited in any of claims 23 to 29, wherein the forming the protective sidewalls uses a gas mixture containing at least one of H<sub>2</sub>, CH<sub>3</sub>F, CH<sub>2</sub>F<sub>2</sub>, CHF<sub>3</sub>, C<sub>4</sub>F<sub>6</sub>, C<sub>4</sub>F<sub>8</sub> as the polymer former and at least one of CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, and NF<sub>3</sub> as the etching gas.

31. The method, as recited in any of claims 23 to 30, wherein the forming the protective sidewalls uses a mixture containing CF<sub>4</sub> and H<sub>2</sub>.

32. The method as recited in claim 31, wherein the CF<sub>4</sub> to H<sub>2</sub> gas flow ratio is in the range of 0.6:1 to 1.4:1 by volume flow rate.

33. The method, as recited in any of claims 23 to 32, wherein the forming the protective sidewalls is selected from at least one of chemical vapor deposition and sputtering.

34. The method, as recited in any of claims 23 to 33, wherein the etch layer is a low-k dielectric material.

35. The method, as recited in any of claims 23 to 34, wherein the via holes are not filled with a sacrificial filler material prior to the start of the trench plasma etching process.

36. The method, as recited in any of claims 23 to 35, wherein the via holes are filled with a filler material to no more than 50% of the via hole height prior to the start of the trench plasma etching process.
- 5 37. A semiconductor formed by the method of any of claims 23 to 36.
38. An apparatus for performing the method of any of claims 23 to 36.
39. An apparatus for etching a layer under an etch mask, wherein the layer is  
10 supported by a substrate, comprising:  
a plasma processing chamber, comprising:  
a chamber wall forming a plasma processing chamber enclosure;  
a substrate support for supporting a substrate within the plasma  
processing chamber enclosure;  
15 a pressure regulator for regulating the pressure in the plasma processing  
chamber enclosure;  
at least one electrode for providing power to the plasma processing  
chamber enclosure for sustaining a plasma;  
a gas inlet for providing gas into the plasma processing chamber  
20 enclosure; and  
a gas outlet for exhausting gas from the plasma processing chamber  
enclosure;  
a deposition gas source;  
an etchant gas source;  
25 a first control valve in fluid connection between the gas inlet of the plasma  
processing chamber and the deposition gas source;  
a second control valve in fluid connection between the gas inlet of the plasma  
processing chamber and the etchant gas source;  
a controller controllably connected to the first control valve, the second control  
30 valve, and the at least one electrode, comprising:  
at least one processor; and  
computer readable media, comprising:  
computer readable code for opening the first control valve for at  
least one deposition step to provide a deposition gas from the deposition gas source to  
35 the plasma processing chamber enclosure;

computer readable code for closing the second control valve for the at least one deposition step to prevent etching gas from the etchant gas source from entering the plasma processing chamber enclosure; and

5 computer readable code for opening the second control valve for at least one etching step to provide an etching gas from the etchant gas source to the plasma processing chamber.

40. The apparatus, as recited in claim 39, wherein the computer readable media further comprises computer readable code for performing the at least one deposition  
10 step and at least one etching step in an alternating fashion for a plurality of times.

41. The apparatus, as recited in any of claims 39 to 40, wherein the etchant gas source comprises an etching gas component source and a polymer former gas component.

15

42. The method, as recited in any of claim 1 to 19, wherein the layer is only a single layer, wherein the feature is etched only in the single layer during the forming the protective coating and etching the feature.

20 43. The method, as recited in any of claims 1 to 19 and 42, wherein the forming the protective coating provides no protective coating on a bottom of the feature.

44. The method, as recited in any of claims 1 to 19 and 42 to 43, wherein forming the protective coating is accomplished using a selective chemical vapor deposition,  
25 which forms the protective coating on exposed surfaces of the etch mask and vertical sidewalls of the feature, but not on the bottom of the feature.

45. The method, as recited in any of claims 1 to 19 and 42 to 44, wherein the etch mask is a photoresist mask, and wherein the forming a protective coating forms a  
30 protective coating that is more etch resistant than the etch mask.

46. The method, as recited in claim 45, wherein the forming the protective coating forms a protective coating of amorphous carbon.
- 5 47. The method, as recited in claim 45, wherein the forming the protective coating forms a protective coating of polyamorphous silicon.
48. The method, as recited in claim 45, wherein the forming the protective coating forms a pseudo hardmask and wherein the forming the protective coating provides no  
10 protective coating on a bottom of the feature.
49. The method, for etching a feature in a layer, as recited in any of claims 1 to 19 and 42 to 48, further comprising:  
forming vias in the layer;  
15 providing the etching mask, wherein the etching mask is a trench patterned mask over the layer, wherein the feature is a trench.
50. The method, as recited in any of claims 1 to 19 and 42 to 49, wherein the forming the protective sidewalls uses a gas mixture containing at least one of H<sub>2</sub>,  
20 CH<sub>3</sub>F, CH<sub>2</sub>F<sub>2</sub>, CHF<sub>3</sub>, C<sub>4</sub>F<sub>6</sub>, C<sub>4</sub>F<sub>8</sub> as the polymer former and at least one of CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, and NF<sub>3</sub> as the etching gas.
51. The method, as recited in any of claims 1 to 19 and 42 to 50, wherein the forming the protective sidewalls uses a mixture containing CF<sub>4</sub> and H<sub>2</sub>.  
25
52. The method as recited in claim 51, wherein the CF<sub>4</sub> to H<sub>2</sub> gas flow ratio is in the range of 0.6:1 to 1.4:1 by volume flow rate.
53. The method, as recited in any of claims 1 to 19 and 42 to 52, wherein the etch  
30 layer is a low-k dielectric material.
54. The method, as recited in any of claims 1 to 19 and 42 to 53, wherein the via holes are not filled with a sacrificial filler material prior to the start of the trench

plasma etching process.

55. The method, as recited in any of claims 1 to 19 and 42 to 54, wherein the via holes are filled with a filler material to no more than 50% of the via hole height prior to the start of the trench plasma etching process.
- 5